STORAGE BATTERIES

(Density 1.1250 really means 1.825.)

STORAGE BATTERIES

A General Treatise on the Physics and Chemistry of Secondary Batteries and Their Engineering Applications

BY

GEORGE WOOD VINAL

Physicist, Bureau of Standards
Member of Amer. Inst. Elec. Eng.

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PREFACE

WITHIN the past ten years, storage batteries have entered into the daily life of millions of people. The name of "storage battery" no longer suggests only the massive stationary cells, familiar enough to the engineer, but almost unknown to others. Small batteries for a great variety of purposes have been developed. Railway trains, electrically lighted by storage batteries, have become universal in express service; electric trucks and industrial tractors, with long records of efficient service, have proved their worth; automobiles by the million now carry storage batteries; farm lighting plants have introduced the storage battery into rural life; and, last of all, the radio receiving apparatus, requiring one or more batteries for its operation, has been instrumental in making storage batteries a familiar factor in every-day life.

The published literature on storage batteries is more extensive than is generally supposed, but the valuable papers are scattered and many are in foreign languages. The author believes, therefore, that the present is an opportune time to present a book of moderate size which summarizes the physical and chemical facts and theories about storage batteries and describes their various applications.

In preparing this volume, emphasis has been laid on the scientific principles involved, without, however, permitting the text to become so technical as to restrict its usefulness. Descriptions of particular makes and types of batteries have been subordinated. The physical and chemical properties of the materials used in constructing storage batteries are discussed in so far as they relate to battery performance, and a general description of the methods of manufacture is given. Especial attention is devoted to the electrolyte and the rôle that it plays. The discussion of the theory is necessarily technical, and perhaps open to criticism by those who still hesitate to accept the "double sulphate" theory. This theory is presented because there is a preponderating amount of evidence in its favor. Brief mention is made of other theories. In discussing the factors which affect the capacity

of storage batteries and the characteristics of the operation, the author has drawn liberally on test reports, and papers published by himself and his collaborators at the Bureau of Standards. The chapter on applications describes only the principal uses of storage batteries. A description of the various kinds of service and the type of battery for each is followed by a statement of the work that the battery has to do and a few records of performance, so far as they are available.

The author was encouraged to undertake the preparation of this book by Dr. S. W. Stratton, formerly Director of the Bureau of Standards, and by Dr. E. B. Rosa, late Chief Physicist of the same institution. He wishes to thank also Dr. G. K. Burgess, Director, and Mr. E. C. Crittenden, Chief of the Electrical Division of the Bureau of Standards, for placing unusual facilities at his disposal. Those of his colleagues who have assisted with valuable suggestions include Dr. H. D. Holler, Dr. J. F. Meyer, Dr. H. L. Curtis, and Dr. F. B. Silsbee.

The manuscript has been reviewed by engineers of several battery-manufacturing and other companies. It is a pleasure to acknowledge the helpful criticisms that have been received. While it is not possible to mention all of those who have thus aided, especial mention should be made of the following: Mr. R. L. Young, American Telephone and Telegraph Co.; Mr. R. C. Mitchell, Edison Storage Battery Co.; Mr. A. V. Morris, Dr. J. L. Woodbridge, Mr. Hugh Leslie, Mr. G. M. Howard, Mr. J. Tracy, and Mr. R. Whitehurst, Electric Storage Battery Co.; Mr. L. T. Beale, John T. Lewis and Bro. Co.; Mr. L. M. Ritchie, National Carbon Co.; Mr. W. E. Holland and Mr. W. H. Grimditch, Philadelphia Storage Battery Co.; Mr. D. S. Funk, Sangamo Electric Co.; Mr. O. W. A. Oetting and Mr. C. Reinhardt, Willard Storage Battery Co. Illustrations have been furnished by the battery companies named above and by the Baker R and L Co.; the Northeast Electric Co.· the Gould Storage Battery Co., and the Prestolite Co., Inc.

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STORAGE BATTERIES

CHAPTER I

INTRODUCTION

The storage battery is typically an electrochemical apparatus and as such must be discussed from three viewpoints. The first is chemical, involving the nature and properties of the materials used in its construction and the reactions which occur during charging and discharging. The second is physical, and this includes a study of the electrical input and output, the factors which affect the capacity, and the theory of the transformation of chemical energy into electrical energy or vice versa. The third viewpoint is the practical one dealing with the engineering applications of storage batteries. There is no sharp line of demarkation between the chemical, physical and engineering aspects, but a full discussion of all is necessary to an adequate understanding of the nature and performance of storage batteries.

The scientific principles underlying the operation of storage batteries have now been so thoroughly investigated, both in this country and abroad, that they may be presented with some degree of confidence. They serve as the groundwork for an intelligent study of batteries as they exist to-day and as a guide for the future development of the art. The presentation of these principles is necessarily technical, but the author has endeavored to make plain the meaning and explain the applications as simply as possible. The more technical and mathematical parts are contained in Chapters IV, VII and VIII. These constitute a relatively small part and may, of course, be omitted by those whose interest lies in other directions. A detailed description of the essential processes of manufacture of batteries and the properties of the electrolyte is contained in Chapters II and III. The factors which affect the capacity of batteries are described in Chapter V. Operation, which includes charging and discharging, the use of rectifiers, battery regulation, costs of operation, and the sources of trouble to which batteries are subject, is contained in Chapter VI.

Chapter IX deals with the principles to be observed in the testing of storage batteries and Chapter X describes in detail the various applications of the batteries and the nature of the service that they perform.

1. THE STORAGE-BATTERY INDUSTRY

The storage-battery industry began with the pioneer experiments of Planté in 1859. The development since that time naturally divides itself into epochs of about twenty years each. During the first of these, the storage battery was little more than a piece of laboratory apparatus, because of the labor and expense involved in preparing and charging the plates. In 1881 a great step forward was taken when the process of forming the active material from the oxides of lead was discovered. This simplified and cheapened the process of manufacture. About this time also, dynamo-electric machines became available for charging the batteries, which had formerly been charged by primary batteries. Invention and investigation were greatly stimulated, but this period was marred by bitter controversies over the relative merits of the different types of batteries, over questions of priority of invention, and over theories to explain the chemical reactions that take place when the batteries are charged and discharged. The batteries of this period were mostly of the stationary variety.

The storage battery was tried in a number of different services early in its history. The first installations often were not successful but they led to valuable results later on. Blizard [1] gives the dates and places of the first installations made in this country, including the following: central station battery at Philipsburg, Pa., in 1885; trolley service at Dover, N. H., in 1893; train lighting battery on the Pennsylvania Railroad in 1882; isolated lighting plant at Baltimore, Md., in 1883; central station telephone service at Chicago, Ill., in 1889. The first successful use of batteries for the propulsion of electric vehicles was stated to have been in 1894, but there were many attempts prior to this date.

The third epoch, beginning with 1900, has been characterized by the development of compact, portable types of batteries and a great increase in the number of batteries used. Portable batteries have been produced for railway train lighting, propulsion of submarines and electric vehicles, starting and lighting of automobiles, signaling on the railroads and in military operations. Stationary batteries have

[1] Electrical Review, 38, p. 75, 1901.

also been developed during this period for stand-by and regulating service, telephone exchanges, and isolated lighting plants. Within the last few years two new applications of importance have appeared. These are portable batteries for radio receiving and for airplane service.

The net result of the development has been to increase enormously the production of storage batteries and to place large numbers of the small sizes in the hands of non-technical people who are quick to appreciate reliable service, but who have little knowledge of the theory or construction of the cells. The growth of the industry since 1909 is shown by the following statistics compiled by the Census Bureau:

TABLE I

Statistics of Storage Battery Manufacture

	1909	1914	1919
Weight of plates, pounds	23,119,331	41,079,047	148,951,766
Value	$4,243,984	$10,651,150	$56,648,347

Since 1919 the rate of increase of production has been greater still. Motor cars in the United States have increased from seven and one-half millions in 1919 to over thirteen millions in 1923. Probably more than three-fourths of these are electrically equipped, requiring a yearly production, for this one purpose, of over six and one-half millions of batteries per year, if it be assumed that the average life of these batteries is from eighteen months to two years. In a less conspicuous way the rapidly increasing use of farm lighting plants and the extension of the telephone have contributed to the phenomenal growth of the storage-battery industry within the past few years.

2. PRIMARY AND SECONDARY CELLS

An electrical battery consists of two or more connected cells which convert chemical energy into electrical energy. The cell is the unit part of the battery, but the word "battery" is sometimes used to mean one cell. The essential parts of a cell are two dissimilar electrodes, immersed in an electrolyte in a suitable jar or container. Familiar examples of electrodes are the copper and zinc plates of a simple primary cell, or the lead and lead-peroxide plates of a storage cell. The electrolyte is a water solution of certain acids, alkalies, or salts which have been found to be adapted to the purpose.

A number of different kinds of cells are in common use. These may be classified conveniently into two general groups as primary and secondary cells. The most familiar of the primary cells is the "dry cell." Secondary cells are generally spoken of as "storage cells" or "accumulators." The distinction between primary and secondary cells is based on the character of the chemical reactions which occur in them when they are in use. Primary cells convert chemical energy into electrical energy and in so doing they become exhausted. Dry cells, when no longer serviceable, are discarded, but some of the so-called "wet" cells may be renewed with new electrodes and electrolyte. These cells cannot be recharged by an electric current because some of the chemical reactions occurring in them are irreversible. Storage cells, on the other hand, convert chemical energy into electrical energy by reactions that are essentially reversible, that is, they may be charged by an electrical current passing through them in the opposite direction to that of their discharge. During this process, electrical energy is transformed into chemical energy, which may be used again at a later time as electrical energy. Electricity is not stored as electricity by these cells. They store chemical energy and so potentially electricity.

There are other cells, some of which are intermediate between primary and secondary cells. These are generally classed with the primary cells for practical reasons, although they may possess some of the essential characteristics of the secondary cells.

This book will be confined to the two types of storage cells which are of practical importance. These are the lead-acid cells and the nickel-iron or alkaline cells. In the former, the plates are of lead and lead oxide, immersed in an electrolyte of sulphuric acid. The nickel-iron cells consist of nickel-plated steel grids containing tubes or pockets to hold the active materials of nickel and iron oxides. The electrolyte for the nickel-iron cells is a solution of potassium hydroxide, more familiarly called caustic potash.

3. THE GROUPING OF CELLS

For most purposes storage cells are used in groups or batteries, the number of cells and their size depending on the service required. Several different arrangements are possible, and it is therefore desirable to arrange the cells in such a way as to secure the most economical service. Two factors are involved in arranging the cells; one is the voltage requirement and the other the capacity. When the cells are connected in series—that is, when the positive pole of one cell is connected to the negative pole of the next, and so on to the end of the row, as

in Fig. 1, the voltage of the cells is additive. Two cells in series will give twice the voltage of one cell, and five cells will give five times the voltage of one, assuming that the cells, taken individually, are of the same voltage. The capacity of a row of series-connected cells, however, is no more than the capacity of a single cell.

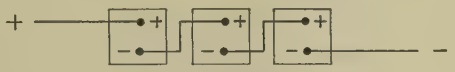

FIG. 1.—Cells connected in series.

Cells may also be connected in parallel, by connecting like poles together, as shown in Fig. 2. The voltage of such a group is no more than the voltage of a single cell, but the capacity of the group is equal to the sum of the capacities of the individual cells. Such an arrangement of storage cells is not commonly made, because it is better to use a single cell of the required capacity rather than a group of small ones connected in parallel.

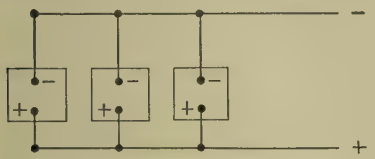

FIG. 2.—Cells connected in parallel.

When more than three cells are involved in a series and parallel connection, there is a choice of arrangement, as shown in Figs. 3 and 4. The cells may be arranged in several rows connected in series, and these rows may then be connected in parallel (Fig. 3), or they may be arranged in parallel groups which are then put in series (Fig. 4). The voltage and capacity of either of these groups is the same, but the former is preferred for storage batteries although the latter is the best arrangement for dry cells. The paralleling of series-connected groups of storage batteries is found in cases where exceptional capacity is required, or for charging when the voltage of the charging source would not be sufficient to charge the cells if they were all connected in series.

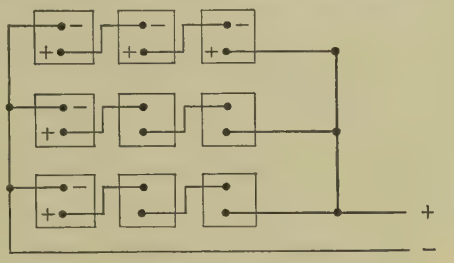

FIG. 3.—Parallel of series-connected cells.

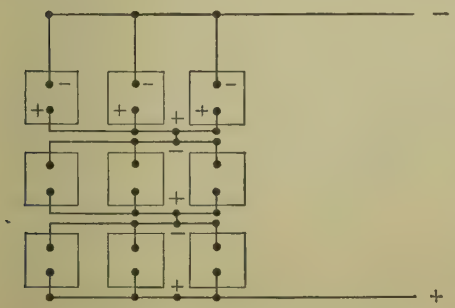

FIG. 4.—Series of parallel-connected cells.

4. ELECTRICAL UNITS

The following electrical units are defined for further use in the pages that follow:

Resistance

The unit of resistance is the "international ohm," which is defined as the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross-sectional area and a length of 106.300 centimeters. It is commonly called the "ohm."

Current

The unit of current is the "international ampere," which is defined as the unvarying electric current which, when passed through a solution of nitrate of silver in water, in accordance with certain specifications, deposits silver at the rate of 0.00111800 of a gram per second. The standard is the silver voltameter.

Electromotive Force

The unit of electromotive force is the "international volt," which is derived by Ohm's law from the international ampere and ohm. Since the standard cell is a more convenient standard to use than the silver voltameter, and accurate determinations of its value have been made,[2] the volt and the ohm are generally used to measure the ampere.

Quantity

The unit for the quantity of electricity is the coulomb, which is equal to one ampere flowing for one second. This unit may also be called the ampere-second. Larger quantities may be measured in ampere-hours. One ampere-hour equals 3600 coulombs.

Energy

The unit of energy is equal to the unit of quantity multiplied by the unit of electromotive force and is called, in electrochemical work, the volt-coulomb. This is the same as the watt-second. A larger unit of energy is the watt-hour.

Power

Power is the rate of expenditure of energy. It is therefore measured in a unit which is the quotient of the unit of energy divided by the unit of time. The name of the unit of power is, therefore, the watt.

[2] Rosa and Vinal, Proc. Nat. Acad. Sci., 3, p. 59, 1917.

CHAPTER II

MATERIALS AND METHODS OF MANUFACTURE

1. HISTORICAL DEVELOPMENT OF THE LEAD-ACID BATTERY

The storage battery of to-day grew out of the investigations of many early experimenters in the field of electrochemistry. Volta's discovery of the galvanic battery in 1800 initiated this line of research. Two years later, Gautherot discovered the polarization of platinum wires, produced by the passage of an electric current through a cell which he used for studying the decomposition of water. He found that a feeble current was returned when he connected the wires after having disconnected the source of current. Ritter repeated Gautherot's experiment in 1803 and went a step farther. He constructed small piles from plates of several metals, including gold and silver. Between the sheets of metal he placed moistened layers of cloth. He charged these piles with an electric current and obtained a discharge current from them after disconnecting the charging source. He thought that the piles stored electricity much as a condenser does, because, like a condenser, the pile had layers of metal of good conductivity alternating with layers of the poorly conducting cloth. Volta showed that this explanation was not correct and attributed the effect to the decomposition of water. Other experimenters entered the field, but it remained for Planté to develop a valuable form of cell as a result of his study of the properties of metals for the accumulation of oxygen.

In 1859 Planté began his study of electrolytic polarization. As a result of his experiments, he devised a battery for the storage of electrical energy, consisting of two sheets of lead separated by strips of rubber and rolled into the form of a spiral. The element thus formed was immersed in a dilute solution, about 10 per cent of sulphuric acid. He studied the charge and discharge of this simple cell and described it as storing the chemical work of the voltaic pile. He found it possible to increase materially the capacity of the cell by a process which is now known as formation. Following periods of charge, he discharged the cell or allowed it to rest for a time, during which local action transformed the covering of peroxide on the positive plate into lead sulphate.

From time to time he reversed the polarity, and repeated the process of charge and discharge to build up the capacity of the cell.

One of the most interesting advantages which this storage cell possessed for the early experimenters was its ability to deliver much larger currents than could be obtained from the voltaic piles. There were serious disadvantages, however, chief of which was the time required for formation. The early literature records the expenditure of two years' time by the manufacturers for the formation of some cells, although others, said to be inferior in performance, received only three months of formation. Primary batteries were the only means available for charging these storage cells, which made the process costly.

Planté's name has been perpetuated in connection with the storage battery by the so-called Planté plate. This type of plate, as distinguished from the others, consists of a sheet of lead on which the active material is formed electrochemically from the lead of the plate itself.

In 1881 Faure [1] patented a process for pasting the surface of the plates with a compound of lead which could more easily be formed into the active materials of the finished battery. He applied a coating of red lead to the surface of smooth lead plates, rolling them together with a layer of flannel between for a separator. This type of cell possessed marked superiority in capacity and ease of formation over the cell of Planté, but the adherence of the active material to the plates was rather poor. It is stated that a battery of this type capable of exerting one horse-power weighed 75 pounds and gave an energy efficiency of 80 per cent.

At about the same time, Brush, an American, also discovered the possibility of preparing the active materials from compounds mechanically applied to the plates. He obtained patents covering this principle.

In the latter part of 1881, Volckmar patented the use of lead plates with numerous holes which were filled with a paste made of pulverized lead mixed with sulphuric acid. Swan [2] also obtained a patent on a grid of cellular structure. These supports for the active material were an improvement over the flat plates which Faure used, but the active material still fell out readily. Sellon patented, in 1882, a modification of the grid to make it hold the material better. He designed his grid in such a way as to lock the active material in place. Sellon is said to have made use of the alloy of lead and antimony

[1] Electrician, 6, p. 323; 7, p. 122, and 249, 1881.

[2] Electrician, 8, p. 142, 1882; British Patent, No. 2272, 1881.

instead of pure lead for this grid. The Correns grid, devised and patented in 1888, consisted of a double lattice of which the bars were triangular in cross-section with the apexes pointing inward so that the active material was held securely in place.

Since 1881 the development of the storage battery has been rapid because of the decreased time required for the formation of the plates and also because of the development of machines for generating electric current. Many of the types of plates and grids which have been devised are of historical interest, but only a few of them are of commercial importance to-day. Detailed descriptions of many of them have appeared in several of the books [3] previously published on this subject, and it is therefore unnecessary to describe them further.

2. PASTED PLATES

a. The Grids.

The grids (Fig. 5) serve as supports for the active material of the plates. The grid of the positive plate has an important part in con-

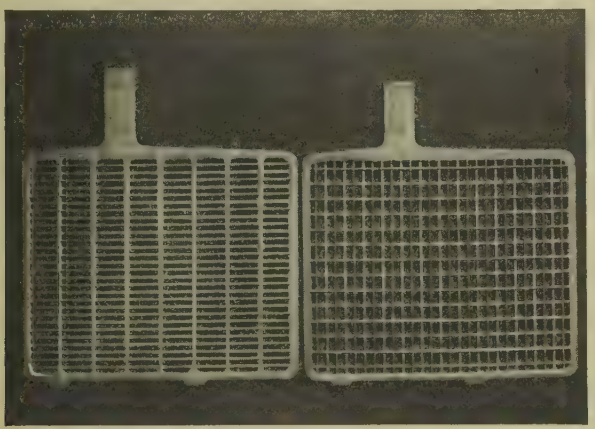

FIG. 5.—Grids for pasted plates, positive on left and negative on right.

ducting the electric current also, since the resistivity of the lead peroxide is about 6 ohm-centimeters, or 300,000 times the value of the resistivity for pure lead. The grids also have an important function in maintaining a uniform current distribution throughout the mass of the active material. If the current distribution is uneven, the

[3] Secondary Batteries, by E. J. Wade, p. 19; Les Accumulateurs Electriques, by L. Jumau, pp. 474, 540 and 997; The Storage Battery, by A. Treadwell, pp. 14 and 50.

changes in volume of the plates, during their charge and discharge, will be uneven, resulting in a tendency of the active material of the plate to crumble. Lighter grids can, in general, be used in batteries designed for discharges of short duration than in batteries for which the discharge is intermittent or extended over a long period of time. The grids are constructed, for the most part, of an alloy of lead and antimony, and frequently have designs which are characteristic of the manufacturer. Other materials have been used for making the grids, including wood. The grids most commonly used at the present time have cross bars which pass either straight or diagonally across the plate and are designed to lock the active material in place.

Materials.—The material used in greatest amount is lead, which is an element having an atomic weight of 207.20. Lead is obtained chiefly from the ore, galena, which is the native sulphide of lead, PbS. The ore in its pure state contains 86.6 per cent of lead, but it is usually mixed with mineral matter and contains other metallic sulphides. The average lead content of the lead sulphide ores mined in the United States is 5.7 per cent.[4] Because the storage battery is affected by the presence of small amounts of impurities, it is of interest to note the more common of the metals and sulphides which occur with it. These include iron, silver, copper, zinc, and arsenic. Galena is widely distributed, being found in nearly all countries. Other ores of lead of less importance are cerrussite, $PbCO_3$, and anglesite, $PbSO_4$.

Lead is a metal, bluish-gray in color, with metallic luster. It oxidizes readily in moist air, becoming a dull gray. The covering thus formed is the suboxide of lead, Pb_2O. Lead in its pure state is soft and malleable, but its ductility and tensile strength are low. Because of its malleability it may be extruded into ribbons and other forms by hydraulic presses. The density of cast lead is 11.33, but this may be slightly increased by rolling. The linear coefficient of expansion is 0.0000292 per degree Centigrade. This is greater than the values for copper, iron, tin, and some of the other common metals. The melting-point for pure lead is 327° C. (620° F.). The resistivity of lead is an important factor in the design of storage batteries. The values given in the literature differ somewhat, probably because lead is very sensitive in this respect to cold working, such as bending, hammering, or drawing. A recently determined value on a cast bar gave 0.0000212 ohm-centimeter at 20° C. (68° F.), or about 12 times the resistivity of copper.

The chemical properties of lead are of great importance in relation to storage-battery performance. Lead is readily attacked by nitric

[4] Mineral Resources, U. S., 1, p. 423, 1914.

acid, but not by cold hydrochloric acid, or sulphuric acid below 1.700 sp. gr. Lead forms a number of important combinations with oxygen, which will be discussed in later paragraphs. Small amounts of many impurities exert a marked influence on the mechanical and electrolytic properties of lead. Traces of arsenic, copper, zinc, and antimony render it harder. Lead, to be satisfactorily rolled, must be pure. The so-called white lead, or alloy of lead and antimony, is less subject to electrolytic corrosion than pure lead.

Lead may be obtained commercially in a high state of purity. Even the ordinary grades of pig lead reach 99.9 per cent purity, and the desilverized lead is still better. For manufacturing storage batteries the highest state of purity is desirable. The grades ordinarily used for this purpose are variously referred to as "desilverized," "refined," or "corroding" lead. The metallurgy of lead is interesting and is of some importance to the battery manufacturer.[5]

The composition of the refined pig leads will vary with the source of the material and the methods used for its purification. "Ordinary common" lead will show about 99.9 per cent of lead, and the best grades will run as high as 99.995 per cent of lead. Between these are the "desilverized" and the "ordinary corroding," or "refined" lead, for which typical analyses are given below:

	Desilverized [6] Lead, Per Cent	Ordinary Corroding [6] Lead (Desilverized), Per Cent
Silver	0.0004	0.0005
Antimony	0.003	0.005
Copper	0.0003	0.0006
Bismuth	0.003	0.050
Iron	0.0015	0.0015
Arsenic	Trace	Trace
Zinc	Trace	Trace
Tin	None	None
Cadmium	None	None
Cobalt and nickel	None	None
Manganese	None	None
Lead by difference	99.9918	99.9424

[5] See Metallurgy of Lead, by Hofman; Lead, by Collins; Handbook of Metallurgy, by Schnabel and Louis, Vol. I.

[6] Thompson, Society of Chemical Industry, 1909; see also Standard Specifications, Am. Soc. Test. Mat.

Suitable methods for the determination of impurities have been described by Scott,[7] and by Schaeffer and White.[8] Standard specifications [9] have now been adopted by the American Society for Testing Materials for the analysis of pig lead.

Antimony, which is combined with the lead in making the grids, is an element having an atomic weight of 120.2. It is obtained chiefly from the ore, stibnite, which is the native antimony sulphide, Sb_2S_3. This ore consists of prismatic crystals, bluish-gray in color with metallic luster. It is often associated with arsenic and bismuth. The color of antimony itself is silver-white with a high metallic luster. It is hard and brittle. The density is 6.69 and the expansion coefficient 0.0000105 per degree Centigrade. Antimony melts at a temperature of 630° C. (1166° F.). The resistivity of antimony is 41.7 micro-ohm-centimeters, or about twice that of lead, and the alloys of the two have a higher resistivity than pure lead. Antimony is not readily oxidized by the air, but it combines directly with chlorine, forming $SbCl_5$. Antimony is oxidized by nitric acid to Sb_2O_3. Arsenic is the principal impurity that is associated with antimony and deleterious to storage batteries.

The percentage of antimony in storage-battery grids ranges from 5 to 12 per cent. Grids are most commonly made, however, with about 7 per cent of antimony. There are a number of reasons for using antimony in this process: (*a*) The material flows better in the mold. (*b*) The melted alloy expands slightly as it solidifies, filling the recesses of the mold and producing sharp castings. Antimony has this peculiar property of expanding, but lead has not. Ewen [10] has shown that the alloy of lead and antimony expands in increasing amounts to a maximum value at about 13 per cent, when solidification takes place. (*c*) The alloy is less subject to electrochemical corrosion and can be used as a support for the active material without losing its strength by being "formed" as the battery is used. (*d*) Antimony increases the stiffness of lead, and also its ductility and tensile strength within limits that are shown in the table. (*e*) The melting-point of the alloy, within the range of compositions used for the grids, is below the melting-point of pure lead. (*f*) The expansion coefficient of the alloy is less than that of pure lead.

Antimony has some detrimental effects, the chief of which is the increased resistance of the alloy as compared with that of pure lead.

[7] Standard Methods of Chemical Analysis, p. 248, 1920.
[8] Chemical Analysis of Lead and Its Compounds, p. 46, 1912.
[9] Serial B35-20.
[10] Jour. Institute of Metals, 4, p. 135, 1910.

Moreover, the antimony may segregate, if present in too high a percentage, which is one of the causes of pitting of the grids and their subsequent growth and buckling.

Some manufacturers prepare their own alloys, but others purchase the alloy in the form of ingots or pigs. The metal should be refined and free from oxide or dross inclosures, and detrimental impurities, such as zinc.

Only one definite alloy of lead and antimony is known. This is the eutectic, having 13 per cent of antimony with a melting-point of about 249° C. (480° F.). The lead and antimony may be mixed in all proportions, however. The alloys of lead and antimony are of great commercial importance because of the wide variety of purposes for which they are used. Many investigations of their physical properties have been made, but very few of these have particular reference to storage batteries. Rosset [11] has determined values for the tensile strength, density, hardness, and resistivity of alloys for battery use, but not all of his results check with those more recently obtained. The metallurgical aspects of the alloy have been discussed by Dean,[12] who has also reviewed the work of many previous investigators, but without reference to the storage battery.

In Table II are found the results of several investigations made at the Bureau of Standards, on the alloys of lead and antimony. The results have been calculated for even percentages of antimony. Undoubtedly, the conditions of casting and the presence of small amounts of impurities may affect the physical properties considerably. The lead used for these investigations was of the grade known as "hardening lead," for which the manufacturer's analysis showed a purity of 99.9947 per cent. The antimony also was the purest that could be obtained.

Casting the Grids.—The molds ordinarily consist of two parts, opening on a hinge. They are made of cast iron or steel, but bronze has also been used in some cases where the filaments of the grids were very fine. Grooves are cut in the opposite faces of the mold, according to the design of the particular plates. Small grids are cast double and later cut apart. Large grids for stationary batteries or submarines are cast singly.

The molds must be evenly heated to make the metal run freely, and they must be provided with suitable vents to let out the air, which is trapped in the mold when the molten metal is poured in. A slight head of the molten metal is required to make it run into all

[11] Centralblatt für Accumulatoren, 6, pp. 138 and 259, 1905; and 7, p. 159, 1906.
[12] Jour. Amer. Chemical Soc., 45, p. 1683, 1923.

the recesses of the mold. The molten metal must be at a high enough temperature, when it is poured into the mold, to prevent premature solidification. After the metal has been poured into the mold, a small amount of water is sometimes added to cool and solidify the alloy. The molds are usually filled from a ladle, by hand, but in a few cases they are filled automatically from the melting pot. Heavy grids, such as those for the Manchester plates, are cast under pressure, the molten metal being blown into the mold by compressed air. The mold is dusted, before each casting is made, with powdered pumice or other powder, such as talc, pulverized mica, plumbago, French chalk, ground soapstone, or lampblack, to facilitate the removal of the finished casting from the mold. In some cases, instead of the more usual dusting process, a smoky flame, to deposit a thin layer of soot, is passed over the faces of the mold.

TABLE II

PROPERTIES OF LEAD-ANTIMONY ALLOYS

Per Cent of Antimony	Temp. of Complete Liquation, ° C.	° F.	Density	Tensile Strength, Lbs. per Sq. In.	Elongation, Per Cent	Hardness Brinell Number	Expansivity Coefficient	Resistivity 20° C. Ohm-cm.
0	327	620	11.33	1780	....	3.0	0.0000292	0.0000212
1	320	608	11.26	....	....	4.2	0.0000288	0.0000220
2	313	596	11.18	....	....	4.8	0.0000284	0.0000227
3	306	583	11.10	4700	15	5.3	0.0000281	0.0000234
4	299	572	11.03	5660	22	5.7	0.0000278	0.0000240
5	292	558	10.95	6360	29	6.2	0.0000275	0.0000246
6	285	545	10.88	6840	24	6.5	0.0000272	0.0000253
7	278	532	10.81	7180	21	6.8	0.0000270	0.0000259
8	271	520	10.74	7420	19	7.0	0.0000267	0.0000265
9	265	509	10.66	7580	17	7.2	0.0000264	0.0000271
10	261	501	10.59	7670	15	7.3	0.0000261	0.0000277
11	256	492	10.52	7620	13	7.4	0.0000258	0.0000283
12	252	485	10.45	7480	12	7.4	0.0000256	0.0000289
13	249	480	10.38	7280	10	.....	0.0000253	0.0000293
14	...	...	10.30	7000	9	.....	0.0000251	0.0000293
15	...	...	10 23	6800	8	.....	0.0000248	0.0000292
16	...	...	. .	6620	6	.....	.....	.....

The melting pot containing the molten alloy is usually fired by gas and contains several hundred pounds of the alloy. During the casting of the grids, the molten metal is stirred from time to time and the dross skimmed off. In the best practice the trimmings from the castings and scrap alloy, unless clean and free from sweepings, are not thrown back into the melting pot, since there is danger of contaminating it with impurities. Ventilation is necessary to carry off the fumes which may sometimes be seen over the melting pot. For this a forced suction through a hood is desirable, since the natural ventilation of the room does not provide satisfactory protection to the workers from poisonous fumes.

FIG. 6.—Magnified section of a defective grid, showing premature solidification of the metal, short runs, webs and bent ribs.

The grids for positive and negative plates are frequently of the same design, composition, and weight; but it is possible to make the negative grid lighter in many cases, because this grid is not required to take as important a part in conducting the current as the positive plate, and it is not as subject to corrosion.

The most common flaws that are observed in grids (Fig. 6) are due to premature solidification of the metal in the mold, to webs which appear when the two faces of the mold do not fit well together, and to warping, which may be caused by mechanical injury in taking the newly cast grid from the mold. The grids are trimmed after casting, to remove rough edges and minor imperfections, but extensive trimming should be unnecessary. Grids for small batteries, such as those used on automobiles, are pasted while still double. After this they

are cut in two, and the lugs, for connecting the grids to the connecting straps, are cut to the proper length and brightened by a scratch brush before the plates are burned to the straps. Large and costly grids containing minor defects are sometimes repaired by burning in new ribs. Before being pasted, the grids must be freed from grease or dirt of any kind.

b. Pasting the Plates.

The pasting of the plates is considered the most secret part of all the manufacturing process. Although a number of patents have been issued for formulas to be used in compounding the paste, comparatively few of the more valuable methods are available even in the patent literature. Many of the published recipes are of little value. The formula for mixing the paste must be adapted to the physical and chemical properties of the lead oxides which are used and since these vary widely, there is little value in a mere recital of formulas. The paste, having the consistency of mortar, is applied to the grids which have been described in the preceding paragraphs, and it is subsequently converted electrochemically into the active materials of the finished plates. Pastes have been made from the various oxides of lead, and also from finely divided lead and lead sulphate, but the oxides are the most used.

Oxides of Lead.—Lead combines with oxygen to form a number of different oxides, the chief of which are lead suboxide, Pb_2O, which is gray in color; lead oxide, PbO, commonly called litharge, which is yellow; lead sesquioxide, Pb_2O_3, which is reddish-yellow; minium, Pb_3O_4, which is red; and lead peroxide, PbO_2, which is dark brown and sometimes almost black. The paste could be prepared from any of these oxides, but litharge has been preferred for the negative plates because it is the most easily obtained and contains the smallest amount of oxygen to be eliminated in the reduction process. Litharge also has the valuable property of forming a cement when moistened with a wide variety of liquids which may be used in preparing the paste. Lead peroxide, although forming the active material of the finished positive plate, is not used in preparing the paste for this plate, because it is not ordinarily available commercially and it is difficult to prepare chemically. An even more important reason is that the coherence of the lead peroxide is poor, so that any paste prepared with it rapidly disintegrates after drying. Minium, or red lead, as it is commonly called, is preferred for preparing the paste for the positive plates. This oxide requires the addition of the smallest amount of oxygen in order to convert it to lead peroxide, and it is easily obtained. The

cementing action of red lead is not as good as that of litharge, but battery red lead contains a liberal percentage of litharge and in some cases litharge is added to it in preparing the paste. The presence of some litharge greatly improves the cementing action of the paste.

Litharge is made by oxidizing melted lead in the air. There is also another form of the lead oxide, called "massicot," which has the same chemical composition but a different physical state. This oxide is formed at a temperature somewhat below the fusion point of the oxide. Massicot, when melted, is converted into litharge. Although the color of litharge is generally yellow, it may at times be reddish, depending on the temperature of formation or the presence of an appreciable amount of red lead.

Minium, or red lead, is prepared by oxidation of lead in two stages. In the first, sometimes called the drossing operation, the lead is oxidized into the form of massicot in a reverberatory furnace through which a current of air is passed. The temperature of the furnace is maintained slightly above the melting-point of lead. The massicot obtained during this process is granular. It is cooled and ground to a fine powder, and then reheated to a dull red, in the air, for a considerable period of time, during which it slowly oxidizes to the familiar form of red lead.

A high state of purity of the oxides used in the manufacture of storage batteries is required. The limiting percentages of impurities for both litharge and the red lead are about the same. A good grade of the oxides for storage-battery purposes would have about the following amounts of impurities:

	Per Cent
Silica	0.05
Calcium monoxide	0.05
Iron	0.02
Copper	0.01
Bismuth	0.05
Silver	0.001
Zinc	Trace
Chlorine	None
Nitrates	None
Arsenic	None

The methods for determining the impurities are described by Schaeffer and White.[13] Moisture is determined by drying a sample of the material at 105° C. Red lead ranges from 68 to 94 per cent of Pb_3O_4, the remaining percentage being chiefly litharge. For storage-batteries purposes, the red lead is confined to the range between 68

[13] Chemical Analysis of Lead and Its Compounds, pp. 25 and 31.

and 78 per cent, but in any case it is desirable that the composition of the material should be constant to within about 4 per cent, because the methods of preparing and applying the paste depend very largely on the physical and chemical properties of the oxides.

The physical properties are fully as important as the chemical properties in the preparation of the paste. The physical properties to be noted are:

(*a*) *Color.*—Litharge may vary from a yellow to a color almost as red as that of the red lead itself. The color is dependent on the method of preparation. Litharge which is cooled rapidly after the lead is oxidized is yellow, and that which is cooled slowly is reddish.

(*b*) *Relation between Fine and Coarse Particles.*—This is a matter of considerable importance, but rather difficult to measure. The measuring may be done with sieves, but a better method is by the use of the Thompson Classifier.[14] Fine particles are said to produce plates of high capacity, but the coarser particles give plates of longer life. A proper balance of fine and coarse particles is, therefore, desirable.

(*c*) *The Apparent Density.*—This is usually measured by the Scott volumeter, and the experiment consists in determining the weight in grams of one cubic inch of the oxide as it is sifted into a small box at the bottom of the apparatus. This anomalous unit of grams per cubic inch seems well established in the industry. The values range from 18 to 30 grams per cubic inch as the apparent density of the red lead, and from 25 to 45 grams per cubic inch for litharge. Storage-battery manufacturers endeavor to obtain material which does not differ by more than 5 grams from their standard. This measurement gives an indication of the uniformity of the product, but does not give any indication of the true density or the relative percentage of fine and coarse particles. The limit of accuracy of this measurement is about one-half gram per cubic inch.

(*d*) *Acid Absorption.*—This may be measured by weighing 5 grams of the oxide into Nessler tubes, adding 50 cc. of N/10 H_2SO_4, and shaking for two minutes, after which a 10-cc. portion is decanted as soon as the liquid clears. This is titrated with N/10 alkali. The difference between various samples is considerable, but the same grade of material should give reproducible results.

(*e*) *True Density.*—The true density may be calculated from weighings of small portions of the oxides suspended in ethyl alcohol in calibrated flasks of 50-cc. capacity. It is, of course, necessary that the portion of oxide be weighed before the alcohol is added.

[14] Proc. Amer. Soc. for Testing Materials, 10, p. 601, 1910.

In addition to the foregoing properties of the material, there are other properties which are of importance in preparing the paste. The lead oxides are practically insoluble in sulphuric acid, and when mixed with certain liquids they form a cement. Litharge exhibits this cementing action with almost any solution of acid, alkali, salt, or even water. Red lead forms a cement with sulphuric acid but not with water. However, it usually contains a sufficient percentage of the litharge to form a cement even when water is used. Another important property of these oxides is their ability to remain a cohesive mass even after the formation of the plate is complete and their chemical and physical condition altered.

Composition of the Paste.—The pastes most commonly used are made from litharge, PbO, or red lead, Pb_3O_4, or a combination of these two oxides made into a stiff paste with sulphuric acid, which may range from 1.100 to 1.250 in specific gravity. When the sulphuric acid is added to red lead, a chemical reaction occurs which results in the formation of lead sulphate and lead peroxide and water. Although this reaction may not be complete so far as the utilization of all the materials is concerned, it probably follows the equation:

$$Pb_3O_4+2H_2SO_4=2PbSO_4+PbO_2+2H_2O. \quad . \quad . \quad . \quad (1)$$

The formation of the lead sulphate is an important factor in binding together the material of the paste. Lead sulphate is also formed when the sulphuric acid and litharge are made into a paste. The following equation suggests the reaction taking place:

$$PbO+2H_2SO_4=2PbSO_4+2H_2O. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is probable that hydration of the lead oxide occurs and that the cementing action is similar to that of plaster of Paris.

Pastes are sometimes made by mixing the oxides with water only. Since the coherence of such a paste, when made from the red lead, is poor after the plate is dry, plates made in this way are commonly dipped in sulphuric acid to form a limited amount of lead sulphate on the surface.

Pastes are also made by mixing the oxides with solutions of magnesium or ammonium sulphate. Such solutions may have a specific gravity of approximately 1.2. It should be noted that these materials, before being made into solution, consist of clear and colorless crystals having a white appearance. The magnesium sulphate is $MgSO_4+7H_2O$ and the ammonium sulphate $(NH_4)_2SO_4$. Commercial grades of these

materials sometimes contain large amounts of impurities and may be gray in color. Such material is not suitable for use in a storage battery. Ammonium sulphate does not react with true red lead, but it does react with litharge according to the following equation:

$$PbO+(NH_4)_2SO_4+H_2O=PbSO_4+2NH_4OH \quad . \quad . \quad . \quad (3)$$

Battery red lead must contain about 25 per cent of litharge in order that this reaction may occur. A considerable amount of ammonia gas, NH_3, is liberated, and the odor can easily be recognized in the pasting room. No lead peroxide is formed during this reaction. The plates retain a pink color instead of turning brown after pasting. In addition to preparing the paste with solutions of these sulphates, manufacturers sometimes mix them with the oxides in the dry form and the paste prepared with sulphuric acid.

So-called hardeners and binders are frequently added in the preparation of a paste, to increase the coherence and hardness of the finished plate. For this purpose, a great variety of substances have been used, the most common of which has been glycerine. Glycerine and litharge together make a cement which is used for many purposes in addition to the preparation of the storage-battery plates. This cement forms an exceedingly hard mass after drying. The proportion of glycerine used in making the paste is ordinarily small. Other hardening agents that have been used include the essential oils, pyridine, tapioca, urea, carbolic acid, and glue.

Another class of materials, called porosity agents, are frequently employed in the preparation of the paste. These are substances which can be subsequently dissolved out of the paste when the setting process has been completed. They are commonly magnesium sulphate, sugar, barium saccharinate, etc.

A third class of materials, called expanders, are frequently added to the paste for the negative plate. Microscopic observations made by Scarpa [15] show that the function of barium sulphate, which is often used as an expander, is to prevent the "soldering" together of the lead particles of the negative plate. There is a tendency for the sponge lead composing the active material to contract and solidify when in service. If this occurs the capacity of the plate is greatly reduced and the battery may become entirely worthless. The expanders consist of inert substances which are insoluble in the electrolyte of the battery and by their presence prevent this contraction and welding together of the lead sponge. Other substances which have been used for this

[15] Electrotechnica, 5, p. 371, 1918.

purpose are lamp black, graphite, ground carbon, and ground wood. If too much of the expanding substance is present in the paste, there will be a tendency for the active mass to grow out of the grid and fall off. It is important, therefore, that the amount of material added should be in accordance with a carefully determined formula.

In addition to the pastes which are commonly used as described above, there are a number of others which deserve brief notice. One of these is the so-called lead sulphate paste, which is made from lead sulphate mixed with ammonium hydroxide, NH_4OH. This paste is made into a thick dough and hardens when dried. The plate is formed in a bath of ammonium sulphate containing a small percentage of free ammonia. In this bath the sulphate can be reduced to the form of lead sponge, and positive plates are prepared by oxidation from the negatives. Glycerol paste consists of approximately 75 parts of litharge mixed with 25 parts of glycerol. This paste forms an unusually hard plate. Lead chloride paste is usually cast in the form required with 10 per cent of zinc chloride. Lead carbonate paste is made from basic or normal lead carbonate and lead oxide, and formed into a paste with an alkaline solution. Negative plates are prepared from this paste by reduction, and the positive plates are prepared by oxidizing the negative plates. Caustic alkali pastes are prepared from litharge mixed with a solution of caustic potash having a specific gravity of about 1.10.

In mixing the paste, the amounts of oxides and other materials are carefully weighed out in the dry form, and to these the solution is added gradually to avoid a sudden thinning of the paste, which sometimes occurs if the solution is added too rapidly. The amount of solution to be added is of importance because the stiffness of the paste has considerable influence on the resulting characteristics of the plate. In order to obtain the thorough mixing required within a relatively short time, dough mixers are commonly used, but these must not contaminate the paste with metallic impurities which would be injurious to the finished battery. Time is an important factor in mixing the paste, since the paste must be put in the grids before the cementing action begins.

The paste is applied to the grids in most cases by hand labor. This is particularly true of the manufacture of plates for starting and lighting batteries. The paste is spread upon the grid with a wooden spatula. Before this is done the plate is placed flat on a smooth table with a sheet of paper interposed between the table and the grid to prevent the active material sticking to the table. Sufficient pressure must be applied to force the paste into intimate contact with the cross bars of the grid. In order to insure a satisfactory plate, the grid must be free

from grease and dirt before it is pasted. The grids are sometimes washed and dipped in a dilute solution of sulphuric acid before the pasting process is begun. Machines of several different types have been devised for pasting plates. The principal advantage claimed for these is the uniformity of pressure with which the paste is forced into the openings of the grid, but it is questionable whether machine-pasted plates have any real advantage over those pasted by hand unless it be in the saving of cost of labor.

After the pasting process is complete, the plates are allowed to dry for periods that vary with the different manufacturers. The drying process is seldom complete in less than one day and usually occupies several days. In order to hasten the drying, the plates may be placed vertically with sufficient spacing to allow for the free circulation of air. Special drying cabinets, through which air is circulated under pressure, are often employed. Some manufacturers dry the plates in ovens at temperatures above the normal room temperature. This hastens the process and may in some cases increase the hardness of the plate. After the drying process is more or less complete, the plates are sometimes dipped in dilute sulphuric acid to increase the amount of lead sulphate which was formed during the pasting process. The time during which the plates are thus immersed in the acid varies from a few minutes in some cases to several days in others. The strength of acid used for this pickling process varies from 1.160 to 1.250 sp. gr.

Character of the Plate as Affected by the Paste.—Soft and porous plates are ordinarily made from soft paste, and the hard plates result from a stiff paste. This effect is clearly shown by experiments of Heim.[16] He prepared four pastes from the same active materials using in each case the same amount of the red lead but varying the amount of the acid, of which the specific gravity was 1.180. He also added a small amount of glycerine in each case. The consistency of the four pastes varied from a stiff paste, such as is ordinarily used, to a thin fluid. After the plates were dried and formed, storage cells were prepared containing five plates, three negatives and two positives, and these were given eight preliminary cycles of charge and discharge. At the end of this treatment the capacity of the four cells, which are designated as A, B, C, and D, was determined to be as follows:

Paste	A	B	C	D
Consistency.....	Stiff paste	Like mortar	Thick fluid	Thin fluid
Ampere-hours.....	28.5	30.2	32.3	34.6

Since the volume of the active material was the same in each case, a

[16] Elektrotech. Zeit., 36, p. 281, 1915.

comparison of the apparent density of the active material in the different positive plates of these cells could be made. It was found that the weight of the active mass of the positive plates of cell D was 16 per cent less than that for cell A, although the capacity of this plate was 21 per cent greater. These results indicate that the porosity of the plates made from the thin paste was much greater than for the others, and it also shows the marked increase in capacity which accompanies an increase in porosity.

The strength of acid used in preparing the paste also has a considerable influence on the porosity of the finished plate. Higher concentrations of acid, as for example those of 1.200 sp. gr., materially increase the porosity. The other materials used in making the paste, as for example the sulphates and oxides, also influence the porosity of the finished plate, as indicated by Jumau. Pastes made from sulphate of lead appear to give the greatest porosity, followed in order by paste made from the chloride, and then by the oxides in order of the decreasing state of oxidation.

The hardness of the plates when finished is influenced by the percentage strength of the acid which was used in mixing the paste and the presence of such substances as glycerine, as described in a previous paragraph. The conditions under which the plate was dried also influence the hardness. Extremely hard plates or extremely soft plates are not desirable. The former suffer as a result of the sulphation which takes place if the batteries are neglected, and they are usually low in capacity when compared with plates of similar size of a softer active material. Soft plates, on the other hand, usually have shorter life than hard plates. The active material is more readily dislodged and thrown to the bottom of the cell during the operation of charging, but the soft plates, by reason of their greater porosity, are not as seriously affected by the formation of excessive amounts of lead sulphate. The measurement of plate hardness has been successfully accomplished by modifying the familiar Brinell test. In preparing the plates for a hardness test they must be fully charged, since the presence of even a small amount of lead sulphate more than that ordinarily present in the charged plate will considerably increase the apparent hardness of the plate. The apparatus used for making the hardness test consists of a bed plate of steel on which the wet plate to be tested can be laid. A $\frac{3}{8}$-inch steel ball is pressed into the surface of the plate by a force of about 7 kilograms. The hardness numeral corresponding to the so-called Brinell test is obtained from the following formula:

$$\text{Hardness Numeral} = \frac{P}{\pi t D}$$

where P = force applied to the ball; D = the diameter of the ball; t = the depth of the indentation. Since t cannot be measured directly, if we let d = the diameter of the indentation, t can be computed from the formula

$$t = \tfrac{1}{2}D - \tfrac{1}{2}\sqrt{D^2 - d^2}$$

The values for the hardness numerals obtained on positive plates found in familiar makes of starting and lighting storage batteries are from 0.45 to 6.5. The plates may be classified according to the following schedule:

Soft plates	0.4 to 0.6
Medium plates	0.6 to 1.25
Hard plates	1.25 to 3.50
Very hard plates	3.50 to 6.5

The faults which are most commonly observed as a result of imperfections in the pasting process are the following: (*a*) Imperfect contact between the grid and paste. This results in the sulphation of the active material at the surface of the grid, and since the sulphate is a non-conductor of the electric current, the active material becomes insulated and cannot be completely charged. (*b*) Cracking of the active material, which is generally due to the shrinkage that occurs while the plates are drying. (*c*) Loosening of the material from the grid. This defect is usually to be attributed to an unsatisfactory formula for mixing the paste. In order to produce the best results the paste should expand very slightly during the drying process. This insures a good bond of union between the grid and the active material. (*d*) Blisters and scaling of the active material, which are caused by the wet paste drying too rapidly on the surface. (*e*) Impurities contained in the oxides or other ingredients of the paste. These are frequently liberated in the electrolyte of the finished battery. An impurity such as copper may then be deposited upon the negative plate and result in local action. Iron, if present, passes into solution in the electrolyte and results in a slow discharge of the battery when standing on open circuit. (*f*) Inequalities in the amount of active material in the finished grids. This defect is due to flaws in the pasting process. The result of these inequalities is buckling of the plates because of the unequal expansion and contraction of the active material during the normal process of charging and discharging the battery. This, however, is only one of many causes of buckling of the plates.

c. Formation of Pasted Plates.

The plates are electrolytically oxidized and reduced in ordinary dilute sulphuric acid or a sulphate solution. The plates which are to

become the positives are made the anode in the forming tank and the plates for the negatives are made the cathode. The word " formation " applies primarily to Planté's process for increasing the capacity of the plates in his cell. This was a process quite different from that used for developing the pasted plate batteries, but the word " formation " is now in common parlance applied to the pasted plates as well. Formation, as applied to the Planté plates, means the creation of a layer of sponge lead on the surface of the negative plates and of lead peroxide on the positives to constitute the active materials of the cell. These active materials are formed from the lead of the plate itself by a series of charges and discharges. Formation of pasted plates, on the other hand, means the oxidation or reduction of the lead oxides or other materials which have been applied to the grids.

The formation process is carried out in forming tanks which are lead-lined, or in vitreous vessels holding several dozen plates. The positives and negatives are usually formed together, although the latter require slightly more time than the former, because a greater number of ampere-hours is necessary to reduce the oxide of lead to sponge lead than to complete the oxidation of the red lead to lead peroxide. A table showing the theoretical number of ampere-hours required for the oxidation and reduction of the various oxides is given on page 28. Some negatives are necessarily formed against dummies because more negatives than positives are used in each cell. The excess averages about 10 per cent. Some manufacturers have made a practice of forming all the positives and all the negatives against dummies, because of the different lengths of time required. This is probably the exception rather than the rule, however, at the present time. The dummies are blank sheets of lead or lead-antimony alloy fixed in position in the tanks.

The time required for the formation varies with the material in the plates and the strength of the current. Formation is seldom complete in a day and it usually occupies several days. The plates to be formed are interleaved together and plates of like kind connected to common terminals. No separators are used between the plates, since the spacing ordinarily employed is sufficient to prevent any short circuits resulting from the active material bridging across from plate to plate. The solution used for the forming process is a dilute solution of sulphuric acid ranging in specific gravity from 1.100 to 1.200. If the solution is too strong it will not be satisfactory in the deeper layers of the active material, and if it is too weak a hydrate instead of lead peroxide will form on the positive plates.

It has been a common practice of some manufacturers of batteries for starting and lighting automobiles and for vehicle propulsion to send

the batteries from the factory in a partially formed condition. The formation of these batteries is completed at the time the batteries are prepared for service by the retailer.

In Europe the forming solutions are frequently made from neutral sulphates. The reasons for using such solutions will appear in later sections. The forming process is attended by considerable gassing of the plates, particularly the dummies, and adequate ventilation of the room in which the forming process is carried on must be provided. The bursting bubbles of gas, as they rise to the surface of the liquid, throw small jets of sulphuric acid spray into the atmosphere. This is a source of discomfort to those working in the room and may cause considerable leakage of electric current between the various circuits if the ventilation is insufficient.

When the plates are first immersed in the forming bath, the lead sulphate which they contain as a result of the chemical reactions occurring during pasting is considerably increased, although the forming process begins as soon as the current is started. Both the minium, Pb_3O_4, and the litharge, PbO, form lead sulphate and water according to the reactions:

$$Pb_3O_4 + 2H_2SO_4 = PbO_2 + 2PbSO_4 + 2H_2O$$

and

$$PbO + H_2SO_4 = PbSO_4 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The sulphation and formation of the plates progress together. During the early stages of the formation the percentage of sulphate increases, but during the latter part of the formation it falls off to a small value. It is obvious from the Equations (4) that the specific gravity of the forming solution will decrease at the beginning owing to the formation of lead sulphate and the liberation of water. Toward the end of the forming period, however, the density of the forming bath rises rapidly and usually finishes higher than its initial value because of the conversion of the lead sulphate which was originally contained in the plates. The following example indicates the general changes which take place in the composition of the material of the negative plate during the forming process.

	Initial Composition	Final Composition
PbO	90 per cent	3 per cent
$PbSO_4$	10 "	2 "
Pb	. .	95 "

Somewhat similar changes occur during the formation of the positive plate. A positive plate pasted with the red lead may be considered to contain a mixture of lead oxide and lead peroxide, since two parts

of the lead oxide and one part of lead peroxide are equivalent to one part of the red lead. Red lead is converted, partially at least, during the pasting process and during its immersion in the sulphuric acid of the forming tank, into lead peroxide and lead sulphate. The following example indicates the changes in composition which occur in the case of a positive plate during the forming process.

Initial Composition		Final Composition
PbO_2	20 per cent	90 per cent
PbO	55 "	7 "
$PbSO_4$	25 "	3 "

The 3 per cent of lead sulphate which remains in the final composition of the plate is of great importance as a binder of the active material. This small percentage of sulphate remaining is not easily removed by excess charging.

Important changes in volume of the active material occur during the forming process. The lead sulphate is considerably less dense than the peroxide or sponge lead of the finished plates. The litharge used in pasting the negative plates is less dense than the lead of the formed material. During the forming process, therefore, the pores of the plate open. This permits the electrolyte to come in contact with the material in the inner recesses of the plate. The porosity which the plate acquires during the forming process is of importance not only in the formation but in the subsequent operation of the finished cell. In the following table are given the densities for the various materials found in the paste and in the finished plates.

TABLE III

Densities of Materials

Material	Formula	Density
Lead	Pb	11.3
Litharge	PbO	9.3
Minium	Pb_3O_4	8.9
Lead Peroxide	PbO_2	8.4
Lead Sulphate	$PbSO_4$	6.3
Lead Chloride	$PbCl_2$	5.8

The current density during the forming process is a matter of importance. The current densities generally used lie within the limits of 0.10 to 0.4 of an ampere per square decimeter (1 to 4 amperes per square foot). The area is reckoned as the apparent surface of the plates. The proper current density to use for any particular kind of pasted plates

depends on the thickness of the active material, on the area of contact between the grid and the active material, and on the density of the forming solution. In general, low current densities are preferable.

It is of interest to consider the oxidation and reduction processes which take place during formation of the positive and negative plates, and to calculate the number of ampere-hours per kilogram of material which are required in accordance with Faraday's law. When litharge, PbO, is oxidized to lead peroxide, one atom of oxygen is added to the PbO molecule. The molecular weight of PbO is 223.2. The amount of oxygen to be added per kilogram of material is, therefore,

$$1000 \times \frac{16}{223.2} = 71.7 \text{ grams.}$$

The electrochemical equivalent of oxygen in ampere-hours per gram is 3.350. This value may be calculated from the following formula: 96,500 coulombs, representing the number of coulombs required for the liberation of 1 gram-equivalent of the substance, multiplied by 2, the valence, divided by 16, the atomic weight of oxygen, and divided by 3600, the number of seconds in one hour. The product of the electrochemical equivalent of oxygen and the number of grams required for the oxidation of the litharge, $3.350 \times 71.7 = 240.2$ ampere-hours per kilogram. Since the reduction of litharge to lead involves the taking away of one atom of oxygen from the molecule PbO, exactly the same number of ampere-hours per kilogram is required for the reduction of one kilogram of material. In the following table is shown the number of ampere-hours per kilogram of material required for the oxidation to the peroxide state or the reduction to sponge lead of the various materials which are used for pasting storage-battery plates. These are the minimum figures and are exclusive of the energy which is wasted by

TABLE IV

AMPERE-HOURS PER KILOGRAM REQUIRED FOR THE OXIDATION AND REDUCTION OF OXIDES, CHLORIDES, AND SULPHATES OF LEAD

Material	Reduction to Lead, Ampere-hours	Oxidation to PbO_2, Ampere-hours
PbO	240	240
Pb_3O_4	313	156
$PbSO_4$	176	176
$PbCl_2$	337	...
Pb	...	449

gassing during the forming process. In calculating the values for minium, it is assumed that Pb_3O_4 represents the composition of the material.

Since the material of the plate at the beginning of the formation process consists of one or more of the oxides and a certain amount of lead sulphate, the following example is given to illustrate the use of the table in computing the theoretical number of ampere-hours which are required for the formation of a negative plate. In this example we shall assume that the plate weighs 300 grams and contains 20 per cent of lead sulphate and 80 per cent of lead oxide. From the table we compute at once that the number of ampere-hours required for the lead sulphate is $\frac{0.20\times300}{1000}\times176=10.6$. Similarly, the number of ampere-hours required for the reduction of the lead oxide is $\frac{0.8\times300}{1000}\times240=57.7$. The total number of ampere-hours required, therefore, for both materials is 68.3. This example may be solved by another method if the electrochemical equivalent of lead is known. By this method the amount of lead in each of the constituents of the paste is calculated. For the lead sulphate this is

$$0.20\times300=\ 60 \text{ grams of } PbSO_4=\ 41 \text{ grams of Pb}$$

$$0.80\times300=240 \text{ grams of PbO} \quad =223 \text{ grams of Pb}$$

$$\text{Total weight}=264 \text{ grams of lead}$$

The electrochemical equivalent of lead is 3.865 grams per ampere-hour. The number of ampere-hours is therefore 264 divided by $3.865=68.3$ ampere-hours, which is the same result as was obtained in working this example by the former method.

The efficiency of the formation process depends largely on the amount of gas which is evolved. Ordinarily the efficiency of the forming process will not exceed 75 per cent. It is necessary, therefore, to add $\frac{1}{3}$ to the figures given above and to the answer obtained in the example, in order to obtain the number of ampere-hours required in ordinary practice. If the formation process is continued beyond the ordinary stopping point, the efficiency will be considerably lower. The elimination of the last traces of sulphate in the plates is difficult and not desirable, since this small amount of sulphate is in effect a cement to hold the active material of the plates together.

The potential relations of the plates during the forming process are of importance, since the potential which must be applied to them multiplied by the number of ampere-hours determines the energy, and

therefore the expense involved in the process. The potential of the negative plates during the forming process is measured against the positive plates or the dummies, which are essentially positive. The potential difference between the negative plates and the dummies increases toward the end of the forming process in accordance with changes in the ionic concentration. The lead sulphate of the plates dissolves to a slight extent in the electrolyte and in dissociating forms lead ions, Pb^{++}. These ions are deposited on the negative plates during the forming process. As they deposit, more lead sulphate dissolves, and when the lead sulphate is almost exhausted near the end of the process, the lead ions become scarce and the potential difference rises to the point where hydrogen ions, H^{+}, are liberated. The potential of the positive plates during formation is similarly measured against the negative plates or dummies in the forming bath. This potential difference is about 2.3 volts at the beginning. This voltage decreases to slightly less than 2 volts after the forming process begins, owing to the decrease in the resistance of the material of the plates. It rises again during the latter part of the formation period to 2.1 volts or higher.

Much gas is evolved during the formation process. The dummies, having practically no capacity, gas continuously. This does not, however, decrease the efficiency of the formation process, but gassing of the plates which are being formed does decrease the efficiency, as mentioned above. The gassing of the plates indicates that the formation process is complete or that the current density is too high. Gassing begins normally at about the time the theoretical number of ampere-hours for the reduction or oxidation of the material in the plates is completed. The conditions which determine gassing depend on the relative number of lead ions, Pb^{++}, and hydrogen ions, H^{+}, in the electrolyte when forming negative plates. Since a scarcity of the lead ions raises the potential of the negative plates, which, during this process, are the cathodes, to a point where hydrogen ions are liberated, it is possible to increase the efficiency of the formation process by maintaining a plentiful supply of the lead ions or keeping the hydrogen-ion concentration low. Some of the manufacturing companies in Europe have, therefore, made use of forming baths which are solutions of neutral sulphates of aluminum and magnesium, because the hydrogen-ion concentration in these baths is much less than in the sulphuric acid solutions. Heating the electrolyte is the only possible way of increasing the concentration of the lead ions, but this loosens the active material of the plates and is not a practicable method. Similar relations with respect to the oxygene volution hold in the forming process for the positive plates. Neutral solutions have been used in Europe in forming these also.

The formation of plates pasted with materials other than the oxides which are ordinarily used is of much less importance, but it is interesting to note that plates have been successfully formed from lead-sulphate and lead-chloride pastes. The plates pasted with lead sulphate are formed very much as in the case of the oxide plates. Since lead sulphate is a non-conductor of electricity, the plates have a very high resistance initially, and the formation begins at the point of contact between the grid and the paste, spreading gradually as the formation progresses. Plates pasted with lead chloride are formed in quite a different way. This paste is soluble and cannot be peroxidized directly, since the lead chloride would go into solution and the lead be precipitated on the cathode with the liberation of chlorine. The lead-chloride paste is therefore reduced in a bath of zinc chloride with a plate of zinc which forms, with the lead chloride, the elements of a primary cell. During this process the lead chloride, $PbCl_2$, is reduced to lead and the zinc becomes zinc chloride $ZnCl_2$.

The positive plates, after formation, may be preserved in the dry state. Negative plates, however, if dried in air will become hot, owing to the formation of oxide, and will again require a prolonged charge before they can be made ready for use. The fully charged negative plates may, however, be preserved in water or they may be placed in the finished cell in the moist condition, provided the cell is sealed to exclude the air.

3. PLANTÉ PLATES

a. Manufacture of Planté Plates.

The essential difference between Planté plates and pasted plates consists in the fact that the active materials of the former are derived from the body of the plate itself, whereas for the latter they are formed from oxides or other pastes which are applied to the plate mechanically. The active materials of the Planté plate are obtained by oxidizing the surface of the lead plate or reducing this material to sponge lead. There is a plate intermediate between the pasted and Planté varieties. It consists of a soft lead grid pasted with the oxides and formed. The active material gradually falls out, but the capacity is maintained by the corrosion of the grid. In this way the plate becomes essentially a Planté plate. Planté plates serve quite a different purpose from the pasted plates. They are ordinarily much larger and heavier than the pasted plates and have a relatively smaller capacity. They are used chiefly for stationary batteries in which considerations of space and weight are of less importance than durability, but they are also used

to some extent for train lighting batteries because these are subjected to severe mechanical conditions. The essential parts of the Planté plates are the underlying portion of lead and the developed surface which consists of a number of leaves or curves designed to increase the surface of the plate and thereby increase the capacity. The effective surface of the Planté plates is 6 to 8 times greater than the apparent surface. The blanks, as the sheets of lead are called before the surface is developed, are prepared by casting pure lead in the form of flat ingots, which are then rolled to the required thickness. Soft lead of a very high degree of purity is required for this purpose. From the rolled sheets the blanks are cut or stamped in accordance with the size and design of the particular type of plate to be made.

A number of different methods are in use for increasing or developing the surface of these plates. One of these is the so-called plowing process. The blank plate is placed in a machine similar to the shaper used in a machine shop. The tool of the shaper is designed to produce a leaf of the proper shape and width. As the lead plate on the movable table of the shaper moves to and fro, the tool plows into the soft lead, making a furrow of the required depth and throwing up on one side a leaf which is parallel to the other leaves. One leaf is produced at each stroke. Ribs to make the plate more rigid are made by jumping the tool at certain points.

A second method of developing the surface of the Planté plates is commonly known as the swaging process. The master swaging block has the design for the plate cut in its surface, the ribs to produce recesses of the finished plate being in relief on the block. The swaging block is pressed against the surface of the soft lead plate while it rocks back and forth and the lead is pressed into the desired form.

A third process for the development of the surface of these plates is called the spinning process. The soft lead plate or blank is held in a frame which reciprocates between revolving mandrels having a large number of steel disks which are pressed gradually into the plate on either side. The lead of the plate flows in between these steel disks, forming leaves with grooves between. The depth to which the steel disk may penetrate the surface of the plate is so regulated as to leave a thin web of supporting material in the center of the plates. Horizontal ribs are obtained in these plates by spinning the plate in sections. Vertical ribs are obtained by spacing washers which are placed between the disks.

Other plates with highly developed surfaces have also been obtained by casting (Tudor plates), but this method is used more in Europe than in this country.

An important type of Planté plate is made by the so-called building-

up process. Heavy grids of lead and antimony are cast with a large number of round holes into which are pressed buttons of soft lead with corrugated surfaces. These buttons, or "rosettes," are prepared from lead ribbon which is extruded by a hydraulic press. The lead ribbon is passed through a crimping machine which crimps the surface, cuts the ribbon to the desired length, and then rolls the piece into the form of a rosette or button. The buttons are pressed into the holes of the lead-antimony grid by a hydraulic press. In order to lock the buttons in place, the holes are made with a slight bevel so that, as the lead button grows during the operation of the cell, it becomes more and more tightly locked in the supporting grid. This type of plate is familiarly known as the Manchester positive.

b. Formation of Planté Plates.

The formation of the Planté plates is an electrochemical process which requires considerable time and the expenditure of a large amount of electrical energy. In the original process used by Planté and generally referred to at the present time as the Planté formation, the plates were alternately charged and discharged, with occasional reversals of the direction of the charging current, until the plates had acquired sufficient capacity. The demand for a more efficient process of formation led to the use of forming agents, which were added to the sulphuric acid solution to hasten the formation by chemically attacking the lead of the plates. This is the method most used at the present time. The formation of Planté plates has also been accomplished by dipping the plates in certain solutions which have a strongly corrosive action on the lead, resulting in a layer of finely divided material which may then be reduced to sponge lead or oxidized to lead peroxide.

When two plates of lead are dipped in a solution of sulphuric acid and an electric current is passed through the cell, a very thin layer of lead peroxide is formed on the plate which is the anode, and the suboxide of lead covering the surfaces of the cathode is reduced to a very thin layer of sponge lead. The evolution of oxygen gas at the anode and hydrogen at the cathode begins almost immediately. If the charging current is cut off, the lead peroxide on the surface of the anode forms a very large number of little primary cells with the underlying lead, so that a vigorous local action begins. Lead sulphate is formed on the surface of the underlying lead, and in a few minutes the plate has lost its charge completely. The sponge lead on the surface of the plate which was the cathode has practically no potential difference from the underlying lead of the plate itself, and consequently no such vigorous local action takes place on this plate. If the charging current is again renewed, a larger

amount of lead oxide is formed on the anode owing to the conversion of the lead sulphate previously formed as a result of the local action on this plate. Each time this process is repeated the amount of lead oxide increases, but in order to obtain an increase in the amount of lead sponge on the surface of the negative plates it is necessary to reverse the current from time to time so that use may be made of the process which occurs at the positive plate. The strength of the sulphuric acid solution which is used has some influence on the amount of oxygen which is fixed on the surface of the anode. Experiments were made by Gladstone and Tribe [17] to determine the amount of oxygen fixed on the

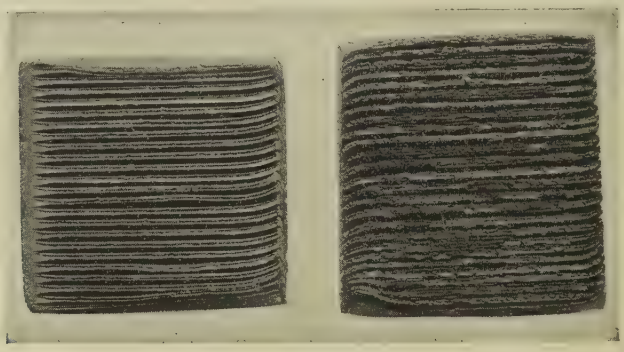

FIG. 7.—Sections of a spun Planté plate before and after formation (C. P. process).

surface of electrodes which were 77 square centimeters in area by the action of one ampere flowing for twenty minutes. The solutions which they used consisted of various strengths ranging from 1 part of acid to 5 parts of water down to 1 part of acid to 1000 parts of water. In the following table the amount of oxygen, expressed in milligrams, fixed by the action of the current for the different strengths of acid is given.

TABLE V

OXYGEN FIXATION

Acid Strength	Oxygen Fixed (mg.)
(Acid to water) 1/5	127
1/10	146
1/50	151
1/100	155
1/500	125
1/1000	Lower oxides and basic sulphates formed

[17] Lumière Electrique 9, p. 25, 1883.

The common method, at the present time, for the formation of Planté plates involves the use of forming agents which attack the lead of the plate. These agents are usually the salts of some acid, such as nitric or acetic, although a number of other substances have been used, including chlorates and perchlorates, chlorides and fluorides, bichromates, permanganates, formic acid, oxalic acid, alcohol, hydroxylamine, and sulphurous acid. The forming process with these addition agents is practically confined to the positive plates, which are the anodes in the forming bath. Negatives are obtained by a reversal of the positive plates and the consequent reduction of the lead peroxide to the sponge-lead state.

In general, the action of the forming agents is to oxidize chemically the lead surface of the plates at the same time that the electrochemical process of peroxidizing the material goes on. The relative strength of the sulphuric acid and the nitric acid or other forming acid is a matter of importance both in determining the depth of the formation and the finishing of the plate. Increasing amounts of nitric acid in the forming bath increase the depth of formation. The current density and temperature also affect the depth of formation. Since the nitric acid is reduced at the negative plate, which is the cathode in the forming bath, any factor, such as increasing current density or increasing temperature, which tends to increase the rate of reduction of the nitric acid, decreases the effective amount of it in the forming bath and thereby decreases the depth of the formation of the plates. Increasing temperature hastens the reduction of the nitric acid by increasing the rapidity with which diffusion takes place. It is apparent, therefore, that during the forming process the amount of the forming agent present in the bath steadily decreases. It is necessary that at the end of the formation it should decrease to zero, in order that the finished plates may not contain traces of the addition agents which would cause subsequent growth and buckling of the plates in service. At the end of the forming period the peroxidizing effect of the charging current must predominate over any chemical action of the addition agents, in order that the plates may be satisfactorily "sealed off." This "sealing off" process consists in completely covering the underlying lead with a peroxide film which serves both as the active material of the plate and as a protective coating. The forming bath is ordinarily a solution of sulphuric acid ranging from 1.050 to 1.150 in specific gravity, to which the forming agent may be added from time to time as the formation progresses. At the end of the forming process the current density is ordinarily increased and the plates, after being removed from the forming bath, are washed and given a further charge in a solution of pure sulphuric acid which is free

from nitrogen compounds or other addition agents. Another method of finishing plates intended for positives is to reverse them in a pure solution of sulphuric acid and water followed by a second reversal to restore the peroxide condition. This process eliminates the forming agent.

While the formation of these plates in solutions of sulphuric acid has been the common practice in this country, an extensive investigation of the use of solutions of neutral sulphates and alkaline baths has been made by Peters.[18]

In some cases plates have been dipped in strong solutions of nitric acid as a preliminary to the forming process. The corrosive action which takes place on the surface of the plates, particularly if the acid is concentrated, results in the formation of complex compounds of lead and nitrates and nitrites which are only slightly soluble in water. The lead plates, having a layer of this material on the surface, can then be formed into peroxide or sponge lead by ordinary forming processes. Another similar method has been to convert the surface of the lead plates into the carbonate.

Schoop is said to have accomplished the primary formation of the negative plates by using a solution of a mercury salt. The negative plates, which are cathodic during formation in this solution, were amalgamated with mercury, and this amalgam was reduced by the electrolytic action of the current, resulting in the formation of a layer of sponge lead on the surface of the plates.

One method of formation of Planté plates which is quite unusual consists in the electrolytic deposition of active materials upon the surface of the lead from solutions of lead salts. This, however, does not constitute the formation of Planté plates in the strict sense of the term.

4. SEPARATORS FOR LEAD-ACID CELLS

The development of thin, porous separators which are placed between the alternating positive and negative plates in storage cells have made possible the development of compact portable batteries. Prior to the use of these porous separators, rods of glass or hard rubber or perforated and corrugated hard rubber sheets were inserted between the plates of the cells to prevent possible short circuits through buckling of the plates. It was not possible, in the early types of batteries, to place the plates close together, because scaling of the active material or

[18] Centralblatt f. Accumulatoren, series of papers beginning 2, p. 293, 1901, and continuing through volume 5.

the formation of " trees " on the negative plates would form a metallic connection between plates of opposite polarity.

The primary object of the separators is to prevent metallic conduction between the plates of opposite polarity while freely permitting electrolytic conduction. The types of separators used at the present time include those made from wood veneer, perforated and slotted separators of hard rubber, the so-called threaded rubber separators, and miscellaneous types made of celluloid, fibrous, or vitreous materials.

a. Wood Separators.

Certain kinds of wood have been found suitable for the manufacture of separators. These include bass, poplar, some kinds of pine, Douglas fir, cedar, cypress, and redwood. The separators are made from a knife-cut or sawn veneer in the form of a long, narrow sheet of the required width. Slots are cut in one side, Fig. 8, leaving a series of narrow ribs, between which is a thin portion called the web. If the veneer has been cut tangentially to the annual rings of the tree the separators are referred to as " rotary cut," while " sawn " separators are cut from quarters of the logs, or radially to the rings. The latter are distinguished from the " rotary cut " separators by the grain of the wood, which in this case appears as a series of bands parallel to the ribs.

Classification of Material.—Wood is divided into two classes, hard wood and soft wood. The hard woods are obtained from trees having broad leaves, while the soft woods are from the conifers, or trees with needles or scale-like leaves. The terms hard and soft often convey an erroneous impression, since some of the soft woods, such as cedar or cypress, are distinctly harder than many of the hard woods, as exemplified by basswood.

The structure of the hard woods differs essentially from that of the soft woods in having some cells which are of much greater diameter than others. Some of these cells are open, forming continuous tubes extending vertically in the tree. These tubes are known as vessels or pores. They are usually visible to the naked eye. The wood structure is composed of a vast number of cells, which are small hollow tubes generally closed at the ends and growing tightly together. The cells that are formed in the spring are of larger diameter than those formed in the summer when the growth of the tree is less rapid. The contrast between the size of pores defines the annual rings which are seen when the tree is cut horizontally to its axis. The rings are plainly marked in such woods as cypress, pine, and Douglas fir, while in poplar, white pine, and basswood they are not so pronounced. The woody fibers, which are small cells with thick walls, provide stiffness and strength.

The cells in the soft woods are so small that they cannot be seen without considerable magnification They differ from the cells and pores of the hard woods, since they serve the double purpose of conducting the sap and providing the strength required by the tree. In some forms of conifers, such as pines and Douglas fir, there are, in addition, canals for the conduction of resin. These extend vertically, and in some cases radially also, among the other cells. Cypress, cedar,

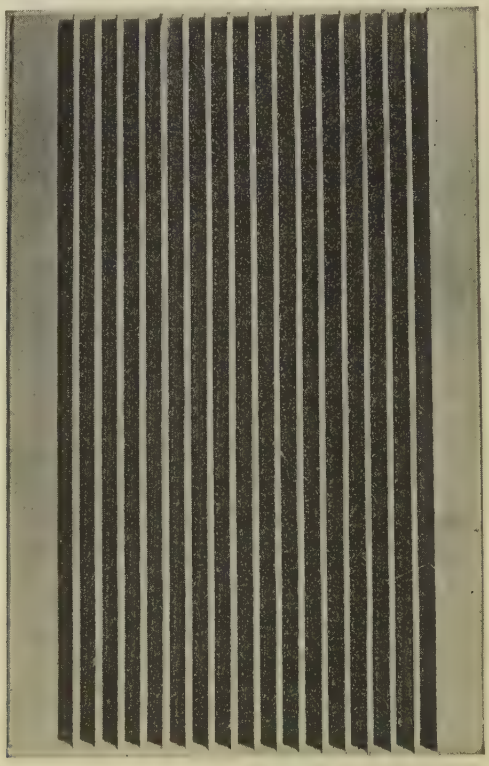

Fig. 8.—Wood separator, showing the grooved Side.

and redwood have none of these resin ducts, but they do contain appreciable amounts of resin.

The different kinds of wood used for storage-battery separators can be identified from their appearance and physical properties before they are immersed in sulphuric-acid solutions. After they have been used in a storage battery it is difficult to identify them. The acid, if of greater specific gravity than 1.250, darkens the wood rapidly. Cherry, which was the first wood used for separators, has a characteristic red-

brown color. Poplar is one of the softer of the hard woods and varies in color from white to a light greenish-yellow. The texture of this wood is uniform and the graining straight. Poplar is sometimes erroneously called basswood. Basswood is cream-white in color, soft, and without any definite figure. The pines are recognized by their characteristic color and the resin that they contain. Douglas fir is sometimes known, as red spruce or Oregon fir. It is distinguished by a reddish color which, however, is not always distinct. Port Orford cedar is extensively used for storage-battery separators and is much like pine in appearance. It grows in the southern part of Oregon and takes its name from a seaport in the vicinity. It has a spicy, resinous odor. Redwood can usually be distinguished by its dark reddish-brown color. It is sometimes confused with red cedar, because of the similar color, but redwood is odorless and tasteless while red cedar has a characteristic odor and a bitter taste. Cypress varies in color and weight, depending on the locality in which it is grown. It presents a waxy or greasy surface. The mechanical properties of these woods are of interest in this connection and reference should be made to tables which have been published by Betts,[19] and by Newlin and Wilson.[20]

The most common defects that are observed in woods used for separators are knots, checks, and shakes. Knots, unless very small, are detrimental in separators. Checks are splits in the log, extending in a radial direction from the center, and are caused by stresses occurring during the seasoning process. A shake is a separation between two annual rings. As a general rule, it occurs in only one part of the ring. Any one of these defects appearing in the finished separator is sufficient cause for its rejection. After the separators have been grooved and cut to size, they should be examined individually before a strong light in much the same way as eggs are candled (Fig. 9). In this way defective separators are easily detected. Because of the frequent occurrence of knots, checks, and shakes, the wastage in preparing separators is considerable.

The principal constituent of wood tissues is cellulose, but with the cellulose are the so-called incrusting layers of lignin and the sap which contains resinous material, tannins, coloring matter, and the various mineral salts. There are a great many varieties of cellulose, but they have certain properties in common.

Celluloses, considered as a whole, are insoluble in the simple solvents and have a composition characteristic of carbohydrates. The empirical

[19] "Timber," p. 10, 1919.

[20] "Mechanical Properties of Woods Grown in the United States," Bulletin No. 556 of the Dept. of Agric., 1917.

formula for them may be written $C_nH_{2m}O_m$. Celluloses resist in various degrees the processes of oxidation and hydrolysis. Generally speaking, however, they are much less subject to oxidation and hydrolysis than the other substances which are closely associated with them in the wood fiber. The woody tissues consisting of cellulose and the incrusting material are frequently called ligno-celluloses. The non-cellulose part of these compounds is generally termed lignin, or lignone. The lignone complex is easily decomposed by hydrolytic or oxidizing agents, yielding acetic acid, which is generally known to be deleterious to the life and performance of storage batteries. For example, wood immersed in

FIG. 9.—Candling separators.

dilute sulphuric acid at 60° to 100° C. readily yields a considerable amount of acetic acid, and the same result is obtained at lower temperatures if an oxidizing agent, such as nitric acid, is also present. The amount of acetic acid that may be formed from the wood varies with the degree of hydration or oxidation of the material. The discussion of the chemistry of cellulose is beyond the scope of this book, but the reader is referred to the book by Cross and Bevin, entitled "Cellulose, an Outline of the Chemistry of the Structural Elements of Plants," 1918.

While it is known that acetic acid in appreciable quantities is harmful to a storage battery, it has been claimed by Skinner[21] that a small quantity of acetic acid is beneficial, rather than harmful, to the negative plate. For reasons that are not fully understood, the presence of wood

[21] U. S. Patent No. 1, 130,640, 1915.

in the battery is beneficial and in some cases necessary for the continued functioning of the negative plates. This may be because of traces of acetic or similar acids extracted from the wood. The wood may be present as separators or be included in the active material of the negative plates. Patents covering the latter procedure have been issued to Chamberlain [22] to Willard.[23]

Treatment.—The wood separators, after being cut to size, are subjected to a chemical treatment which has for its object the removal of soluble and easily hydrolized matter, and the expansion of the pores. Many different methods have been used, most of which are covered by patents. Some of these methods have been based on the methods used for the preparation of wood for paper-making. In general, the treatment consists of the removal of the mineral salts and other soluble matter contained in the sap, as well as the easily hydrolized parts of the ligno-cellulose, by the use of steam, boiling water, or dilute solutions of various chemical reagents, including caustic soda, sodium bisulphite, sodium sulphite, and sulphuric acid. The proper regulation of the solutions, including the concentration, the temperature, the time of immersion, and the subsequent washing of the separators, requires skill and experience. Insufficient treatment means high electrical resistance in the battery and incomplete elimination of deleterious substances; excessive hydrolysis, on the other hand, means an unnecessary loss in the mechanical strength of the separators. As the separators are wedged tightly between the positive and the negative plates of the cell when in service, the question of mechanical strength is of importance. The plates expand during discharge and contract when charged, subjecting the separator to stresses in addition to the severe chemical conditions imposed on it.

Many efforts have been made to prepare separators from materials other than wood. The most notable of these is the so-called threaded-rubber separator (Figs. 10 and 11) patented by T. A. Willard.[24] These separators consist of thin sheets of rubber containing several hundred thousand threads passing through the thin sheet of rubber from one side to the other. These separators are made from a block which is built up of alternate layers of the porous material and rubber and then cut transversely into thin sheets. These separators are mostly used in batteries for starting and lighting service on automobiles, and permit the manufacturers to send out the batteries in the so-called bone-dry condition. The batteries, therefore, are not subject to discharge and

[22] American, 1,379,900, 1921.
[23] British, 155,944, 1919.
[24] U. S. Patent 1,375,763, 1921; Electrician, 86, p. 355, 1921.

sulphation before being put into use. This obvious advantage, made possible by a separator which would not warp and split when dry, as does the ordinary wood separator, led to the development of the so-called moist separator batteries containing wood separators. It was found that storage cells containing wood separators could be shipped with the plates dry and the separators moist, and stored for indefinite periods of time, provided the cells were sealed to prevent the escape of moisture or access of air, which would cause the formation of lead oxide on the negative plates.

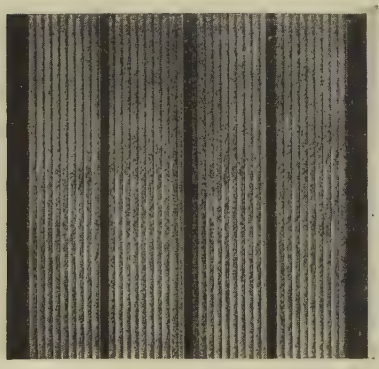

FIG. 10.—Threaded-rubber separator.

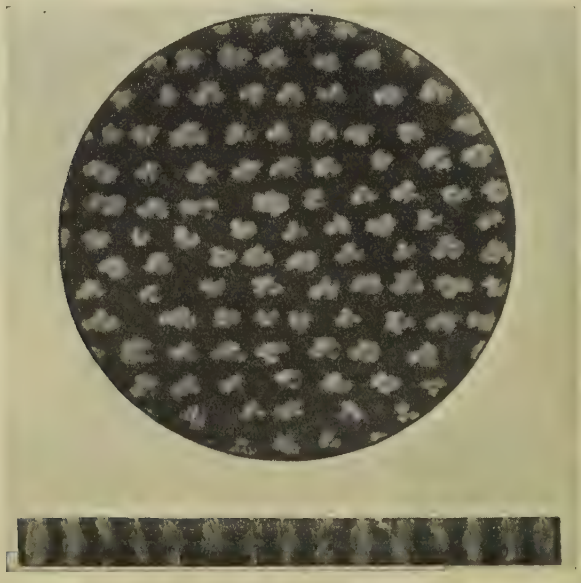

FIG. 11.—Microscopic section of a threaded-rubber separator; side view magnified 100 times (above) and cross-section magnified 150 times (below).

b. Other Separators.

Other forms of separators have been made of volcanic ash, powdered glass, and powdered silicates with or without binders. Still another

form of separator consists of celluloid sheets with a series of V-shaped passages punched in them to permit the free passage of the electrolyte. Such a separator was patented by Luthy.[25] Comparatively few of these miscellaneous types of separators have survived the test of practical use.

Much effort has been expended to provide means of improving the life of the wood separators used in storage batteries. The separator is

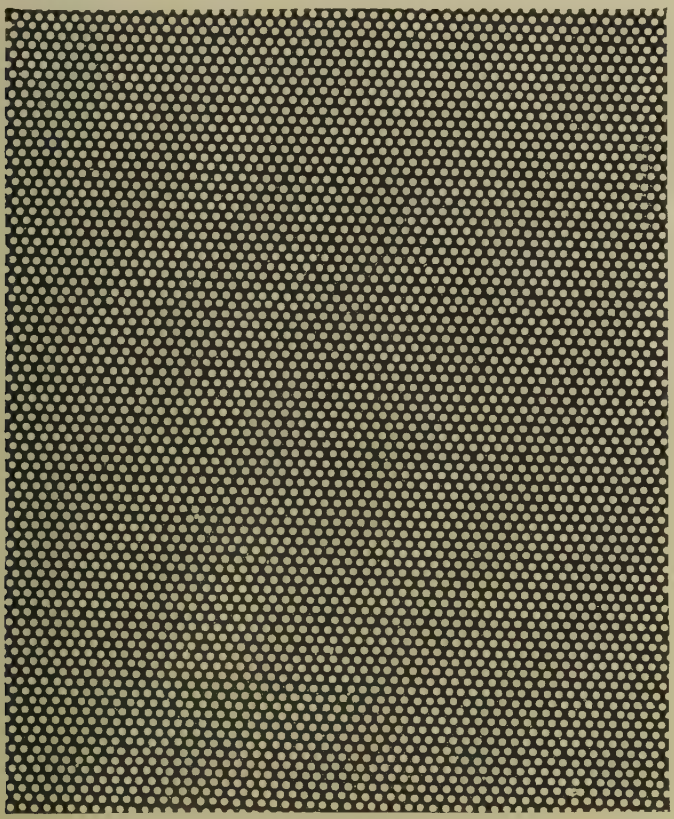

FIG. 12.—Perforated hard rubber separator.

subjected to the action of acid, which weakens the woody fibers, and it is in close proximity to the positive plate, the active material of which is a powerful oxidizing agent. Chamberlain[26] has patented a separator impregnated with a thin film of unvulcanized rubber. The rubber is applied in such a way as to cover the surface of the inner

[25] U. S. Patent 1,305,657, 1919.

[26] U. S. Patent 1,328,420, 1920.

fibers without stopping the pores. In some types of batteries it has been found possible to protect the wooden separators from the action of the lead peroxide of the positive plates, and at the same time to hold the active material of these plates in place, by the use of perforated or slotted rubber separators in addition to the wood separators. These consist of thin sheets of rubber, as illustrated in Figs. 12 and 13. The perforated separators contain many small round holes, while the slotted separators contain rows of narrow slots about $\frac{3}{16}$ inch long. The advantage claimed for the slot is that because of its narrowness it prevents particles of the active material of the positive plate from falling out, without unduly increasing the internal resistance of the battery.

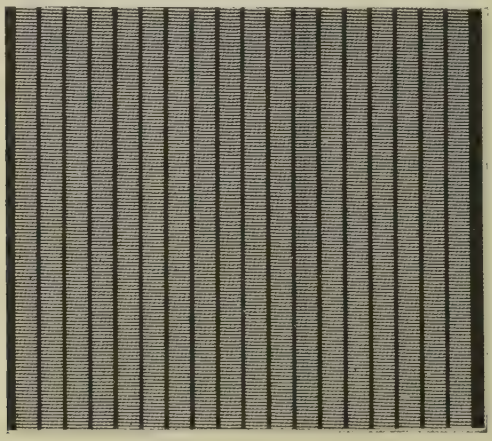

FIG. 13.—Slotted hard rubber separator.

The percentage of material punched out in these slotted and perforated separators is a matter of considerable importance in determining the performance of the battery. If too much material is punched out, the rubber separator is weak and liable to breakage. If too little material is punched out, the resistance of the cell is materially increased. It has been found possible to use the perforated and slotted rubber separators in batteries of the vehicle type, signal batteries, and batteries for submarine propulsion. For these the porosity ranges from 18 to about 25 per cent, by which is meant that 18 to 25 per cent of the material of the separator has been punched out in the form of round holes or slots. This is not sufficient for batteries used for starting automobiles, since these batteries are required to give excessively large currents during the period of cranking the engine. Slotted separators for which the porosity

is approximately 40 per cent are now available for this purpose. One of these is shown in Fig. 13.

c. Relation of Design to Cell Performance.

The grooved side of the separator is always placed next to the positive plate. This is done for several reasons. The actual contact of the separator with the highly oxidizing material of the positive plate is minimized and a greater volume of acid, for use by the positive plate during discharge, is provided. At high rates of discharge, the maximum capacity of the positive plate is attained only for moderately high concentrations of the acid. It is necessary, therefore, that the positive plate should have an ample supply of acid to maintain the concentration. The negative plate, on the other hand, reaches its maximum capacity at a relatively lower concentration. The flat side of the separator helps to retain the active material of the negative plate in place and limits the amount of acid available for the use of this plate. If the back of the separator is perfectly smooth the amount of electrolyte available for the negative plate may be too small, and it has been the custom of some manufacturers to leave the backs of the separators rough and unfinished in order that more acid space might be provided.

The proper thickness of the separators is determined by the use for which the battery is intended. Starting and lighting batteries for automobiles, which are required to deliver large currents, must necessarily have a low internal resistance. These require relatively thin separators, commonly $\frac{5}{64}$ inch in thickness. Signal batteries, on the other hand, for which the rates of discharge are small, are provided with thick plates and a relatively wide separation. Separators for these may be as much as $\frac{1}{4}$ to $\frac{3}{8}$ inch in thickness measured over the ribs, but the web of such separators is relatively thin.

Wood separators are now commonly used in stationary batteries also, including those with Planté plates. Separators for such batteries usually consist of flat sheets of veneer reinforced with dowel pins, which are slotted and inclose the separator at its outside edges and in the middle also. Grooved wood separators are also used.

d. Flat Separators.

The Exide-ironclad batteries contain separators differing from any of the forms previously described. These separators are flat sheets of wood without grooves. The construction of the positive plates provides the space required for the acid, and the rubber tubes serve the double purpose of a rubber separator and a retainer for the active material of

the plate. The rubber tubes are slotted along the side to provide access for the electrolyte to the active material, but as these slots are exceedingly narrow, the lead peroxide within cannot escape.

e. Electrical Resistance.

The resistance to the passage of the electric current through the separators is an important quantity, varying with the kind of wood of which the separator is made, the treatment which it has received, and the direction of the grain of the wood. In general, it is known that woods such as basswood and poplar have a lower resistance when saturated with electrolyte than cedar or cypress. Tests are commonly

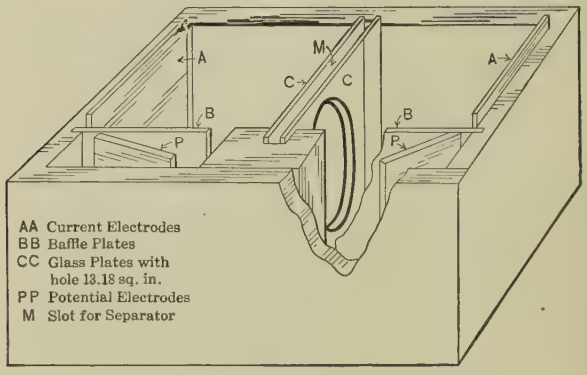

FIG. 14.—Cell for measuring resistance of separators.

made at high rates of discharge to determine the voltage characteristic of the battery, since this in turn depends on the internal resistance of the battery and so upon the separator resistance. It is desirable to have more direct measurements of the separator resistance, however, and a method has been devised for measuring the resistance of individual separators.

The method consists in measuring the electrolytic resistance of a specially constructed cell, with and without the separator interposed across the path of the current, under otherwise comparable conditions. The difference of the two measurements gives the effective resistance of the separator. The cell which is shown in Fig. 14 contains two negative plates at the ends of the cell which serve as current terminals, and two other plates set at an angle are used to measure the potential drop across the separator which divides the cell at the middle. The separator is inserted between the glass plates, which have a fixed circular opening. A 60-cycle alternating current is used to avoid polarization

effects. The electrical circuits are shown in Fig. 15. A transformer with two secondary windings of 5-ampere capacity was used to reduce the 110-volt circuit to about 10 volts. The current from one secondary was passed through the cell and maintained at 5 amperes. The current from the other secondary was passed through a calibrated slide wire and a non-inductive resistance of about 100 ohms. This circuit served as a potentiometer in phase with the current through the cell. An alternating current galvanometer was used to determine the balance, care being taken to maintain the field of the galvanometer in phase with the potentiometer. The accuracy of the measurements was tested by measuring the value of a known resistance. The resistance of individual

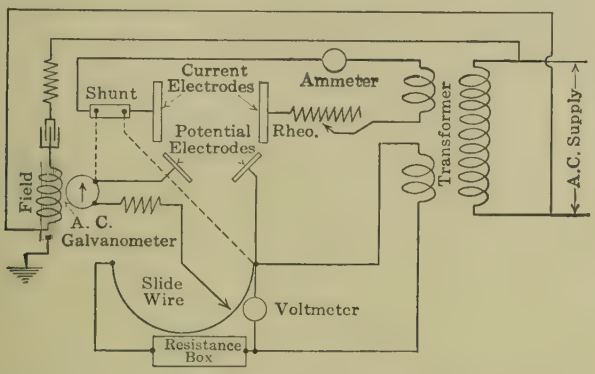

FIG. 15.—Circuit for measuring the resistance of separators.

separators, from the same lot and similarly treated, varied from 5 to 15 per cent, but the accuracy of the measurements was probably good to about 1 per cent. Several weeks' immersion in sulphuric-acid solutions is required prior to the measurements, in order that the resistance may reach a constant value.

The resistance of the separators is expressed as the resistance per square inch or per square decimeter of surface. To apply the figures of Table VI to a particular case, it is necessary to estimate the area of the separators within the cell and to divide the figures which are given by this factor. For example, if there are 100 square inches of separator surface, the resistance will be $\frac{1}{100}$ of the value given for the particular kind of wood. Two values are given for redwood and cedar because of the different methods of cutting the samples. These indicate that the resistance of the sawn separators is somewhat less than that of rotary-cut separators of the same kind of wood.

The porosity of the separators is an important factor in determining

the physical performance of storage batteries, since it affects not only the internal resistance, but also the equalization of the acid concentrations during charge and discharge. The resistance of the separators depends on the length and cross-section of the pores and indirectly on the direction of grain of the wood. As an approximation, it may be assumed that the porosity of the wood is inversely proportional to the resistance. No standard of porosity has been established for the determination of quality of the separators.

The figures given in Table VI are for separators of the type used in starting and lighting batteries. The separators had 16 ribs and 17 slots. The thickness of the backweb was 0.052 inch; the thickness over the ribs, 0.085 inch; and the mean thickness, 0.063 inch. All of these separators had received the same treatment.

TABLE VI

Resistance of Storage-battery Separators

Each figure is the mean of observations on four samples of each kind. The separators were allowed to stand for twenty-three days in sulphuric acid of 1.280 sp. gr. before being measured. The resistances are expressed as the resistance per square inch of surface in the electrolyte of specific gravity 1.280 at 22° C.

Wood	Cut	Resistance in Ohms	
		Per Square Inch	Per dm².
Poplar	Rotary	0.040	0.0026
Cherry	Rotary	0.042	0.0027
Basswood	Rotary	0.054	0.0035
Redwood	Rotary	0.084	0.0054
Redwood	Sawn	0.063	0.0041
Cedar	Rotary	0.084	0.0054
Cedar	Sawn	0.057	0.0037
Fir	Rotary	0.116	0.0075
Cypress	Rotary	0.124	0.0080

f. Effect of Acid on the Wood.

In judging the quality of wood separators, it is of importance to determine the effect of acid on the wood as well as to determine the electrical resistance. Sulphuric acid chars the wood, as may readily be observed. The extent to which this action takes place depends very largely on the concentration and the temperature of the acid. When the specific gravity of the acid is 1.250 or below, the charring action is

relatively slight, even when the wood is immersed for a long period of time. At 1.300 the charring action is noticeably greater, and it becomes serious at concentrations higher than this. A series of experiments has been carried out at the Bureau of Standards [27] to determine the decrease in strength of several kinds of wood as a result of being immersed in several concentrations of acid for a period of twenty-one weeks. Samples in the form of strips were cut from separators of different kinds of wood, all of which were of the same thickness and method of treatment.

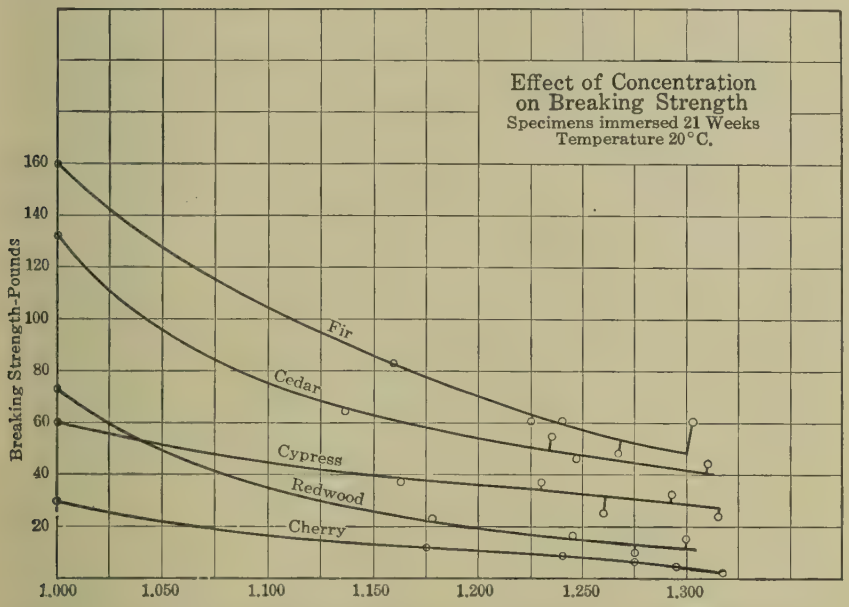

FIG. 16.—Curves showing the decrease in breaking strength of separators when immersed in electrolytes of increasing specific gravity.

Each strip included two ribs and the web portion between. The samples were kept in the solutions at a constant temperature of 20° C. (68° F.) for the duration of the experiment, and they were then taken out and subjected to tensile-strength tests while still wet. The results of this experiment are shown in Fig. 16. Each point is the mean of four determinations. A similar set of specimens were kept at 45° C. (113° F.). The breaking strengths for these averaged about one-half the values for the corresponding points at 20° C., as shown in the figure. The effect of the acid in weakening the wood fiber is clearly shown in the falling of the curves.

[27] Bureau of Standards Technologic Paper.

5. CONTAINERS FOR LEAD-ACID CELLS

a. Rubber Jars are commonly used for the containers of starting and lighting, vehicle, portable, and submarine cells. Rubber is a general name applied to a variety of natural gums obtained from certain species of tropical plants. The biscuits of crude rubber are ground, washed, dried, and mixed with fillers and sulphur, after which the material is calendered. When the mixture is heated to a temperature above 120° C. a combination of rubber and sulphur takes place, with the formation of a new substance of markedly different mechanical properties. This process is called vulcanization. The degree of vulcanization varies with the proportion of sulphur, the temperature and duration of the heating. The quality of the final product, as, for example, the battery jars, depends on these factors and also on the percentage of rubber in the compound. It is, therefore, not surprising that the qualities of the jars upon the market should differ widely. The jars may be molded or made by the "building-up" process. By the latter process the sheets of the unvulcanized rubber compound of appropriate thickness are placed upon a cast-iron mandrel. The bottom strip is placed in position first. The sheet to form the sides is wrapped around the mandrel, and all seams are lapped and rolled until the surfaces are in intimate contact. The jar is then vulcanized. After the jar has been removed from the mandrel it is trimmed and ground to the exact dimensions for the height required. The molded monobloc containers for certain types of batteries are now superseding the use of the individual jars.

The covers are molded. These differ greatly in shape and arrangement of the openings. Covers for the smaller cells, such as for starting and lighting batteries, vehicle batteries, etc., generally have three holes in the cover; two of these are for the protruding terminal posts and the third for the combined vent and filling aperture. The sealing compound is a blown oil asphalt with a melting point of about 200° F. The softer compounds melt below this temperature and the harder ones above it. As the compounds contain volatile constituents which are driven off if melted for any considerable time, thereby changing its physical properties, it is not desirable to use the compound a second time.

The method of sealing the terminal posts at the point where they pass through the cover is a matter of great importance. Unless the posts are satisfactorily sealed, they are likely to work loose in the cover and cause leakage of the electrolyte. Each manufacturer has his own design for locking the post and cover together, but not all of these have been found satisfactory. Three of the familiar arrangements are shown

in the illustration, Fig. 17*a*, *b*, *c*. The sealing nut of rubber or lead alloy is screwed down on the post, pressing the cover against a soft rubber gasket underneath. Covers for starting and lighting batteries and vehicle batteries are almost universally of rubber, but for isolated plant batteries, and some other forms, they are also made of lead-antimony alloy or glass. The covers, when made of rubber, are not necessarily of the same quality as the material of the jars.

The vent plugs in common use are of three kinds, the bayonet, the screw type, and the soft rubber plugs. The bayonet type is fastened in place by a partial turn; the screw type, on the other hand, is threaded, as its name implies. Soft rubber plugs are pushed into place. The

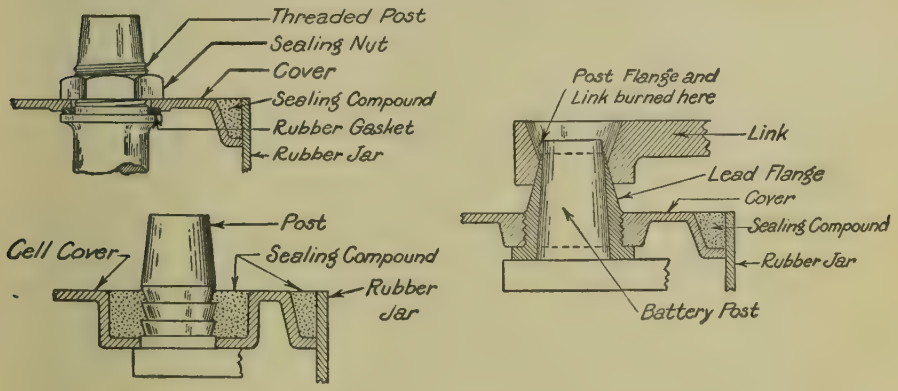

FIG. 17.—Three methods of sealing the terminal posts.

vent plugs provide for the escape of gas during charging, and by removing the plug a larger opening is provided for filling the cell with electrolyte or water. Since the vent plugs provide free access of the air to the interior of the cell, electrolyte may be spilled through the vent if the battery is inverted, and some sloppage may occur because of shock. The method of overcoming this difficulty most frequently used on batteries for automobiles is to insert in the vent plugs a baffle plate which effectively prevents sloppage or the escape of electrolyte during charging under the ordinary conditions of service. Batteries for certain kinds of signal service and for use on airplanes are required to be of the non-spill type. Various valves, to permit the free escape of gas without liquid when the battery is inverted, have been devised, but none have come into common use. The arrangement of the "double chamber" has also been employed for this purpose. The double chamber is an upper compartment, sufficiently large to hold all of the liquid in the cell. The vent plug is elongated and the hole at its lower tip is so

placed as to be out of the liquid whatever position the cell may be in. This is an effective device, but has the disadvantage of increasing the size and weight of the cell. The electrical resistance is also increased because of the extra length of the terminal posts that are required. A picture of a double-chamber cell is shown in Fig. 107 in chapter on Operation.

The quality of rubber jars has been greatly improved within recent years. The qualities desired are strength and toughness, to enable the jars to withstand ordinary shocks without breaking; the jars should not soften excessively at temperatures of 65° C., nor become too brittle at −15° C. since these temperatures are within the range of service conditions; they must be water-tight and impervious to the action of sulphuric-acid solutions. Breakage of jars in service is a serious and annoying occurrence, but this is much less common now than formerly.

A recent development in the starting and lighting battery industry has been the development of the "monobloc" or unit containers of rubber. These rubber boxes, with partitions to inclose the individual cells, combine in one piece the individual jars and the tray of the ordinary battery. Standards of size, but not of quality, have been adopted for these. Some are found more satisfactory than others; the chief point of failure is the distortion of the box, with resulting leakage of electrolyte, that may be caused by the pressure of the hold-down clamps when the battery is warm. It is possible to design the box so that this difficulty may be avoided.

b. Celluloid Jars.—Celluloid is a plastic material prepared from cellulose nitrate and possessing good mechanical properties. It is transparent, light in weight, may be machined or molded, and is not attacked by dilute acids. It has, therefore, found some use in the manufacture of storage-battery jars, but it possesses two serious drawbacks for this purpose. It is highly inflammable, and leakage of electrolyte may occur at the seams. The seams are cemented together by the use of glacial acetic acid or by a solution of celluloid in amylacetate. The use of celluloid jars has been more common in Europe than in America. Investigation of the causes of several fires occurring in batteries equipped with celluloid jars has shown in one case clear evidence that the celluloid was ignited by the heat generated at a broken terminal post. A less inflammable substitute for celluloid is made from cellulose acetate, but it is not known whether this can be satisfactorily used for storage-battery jars.

c. Glass Jars are very commonly employed for stationary batteries except for the largest sizes. Desirable qualities in the glass jars are

transparency, freedom from attack by the acid, the absence of blow holes and the ability to withstand temperature variations.

d. Lead-lined Tanks are used for large stationary batteries and train-lighting batteries, and are generally applicable where considerations of space and weight are not of importance. The wood casing must be of good quality, since the lead lining has little mechanical strength and is liable to deformation. The best wood available is a resinous long-leaf yellow pine. The upper rim of the lead lining is usually reinforced and is called the crown. The lead lining should be extended over the top and down the side a short distance with drip points at intervals. The lining may be either of pure lead or of the alloy with antimony. Data are given in Table VII for the weight of the sheet material, including pure lead and the alloy of lead and antimony.

TABLE VII

WEIGHT OF SHEET LEAD AND THE ALLOY OF LEAD AND ANTIMONY IN POUNDS PER SQUARE FOOT

(Calculated from the dimensions and densities given in Table II)

Thickness in Inches	Pure Lead	Alloy 4 Per Cent Antimony	Alloy 8 Per Cent Antimony
1/16	3.6	3.5	3.4
1/8	7.2	7.0	6.8
3/16	10.8	10.5	10.2
1/4	14.4	14.0	13.7
5/16	18.0	17.5	17.1
3/8	21.6	21.1	20.5
7/16	25.2	24.6	23.4
1/2	28.8	28.1	27.3
5/8	36.0	35.0	34.2
3/4	43.2	42.1	41.0
1	57.7	56.3	54.8

6. TYPES AND SIZES OF PLATES FOR LEAD-ACID CELLS

In the previous discussion the pasted and Planté plates have been described in a general way. No further description of the flat pasted type of plate is necessary. Typical plates of this type are shown in Fig. 18. Some of the other forms which are in commercial use will be described here.

The Exide-ironclad positive plate is used in vehicle, locomotive, and submarine batteries and for other uses where ruggedness and light

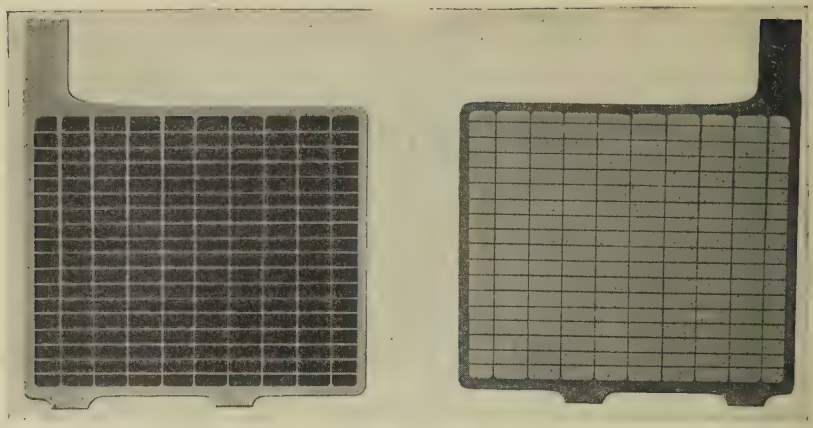

FIG. 18.—Pasted plates of the type for starting and lighting batteries; positive left, negative right.

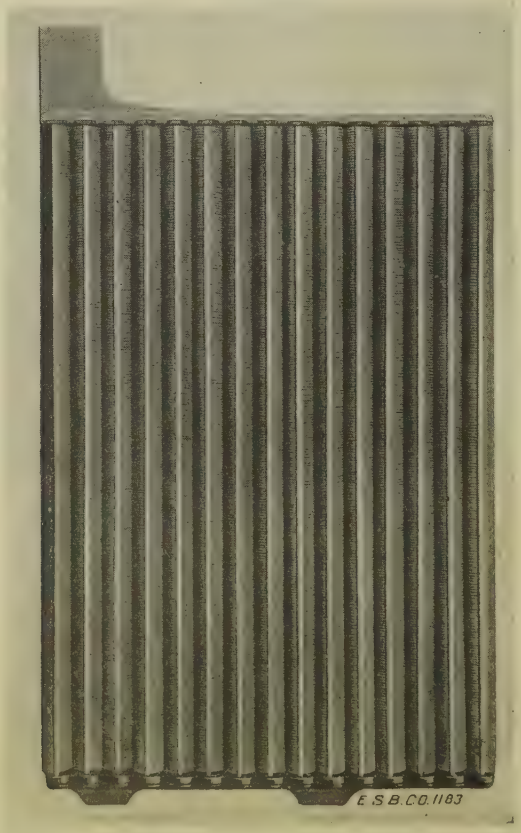

FIG. 19.—Exide-ironclad positive plate.

weight are desired. The grid of this plate is composed of a number of parallel vertical rods of the lead-antimony alloy, which are burned to supporting frames at the top and bottom. Each vertical rod forms the core of a pencil consisting of the active material inclosed within a hard rubber tube having a large number of horizontal slots. The slots provide access of the electrolyte to the active material but prevent the active material from being washed out. The rubber tubes at the outside edges of the plate are reinforced by leaving the exposed edges solid. Each tube has two vertical ribs projecting on opposite sides at right angles to the plate. These ribs reinforce the tubes and also serve the purpose of insulating spacers, taking the place of the ribs on the wood separators. A plate of this type is shown in Fig. 19. The negative plate for the Exide-ironclad is a flat pasted plate differing from the ordinary type chiefly by being

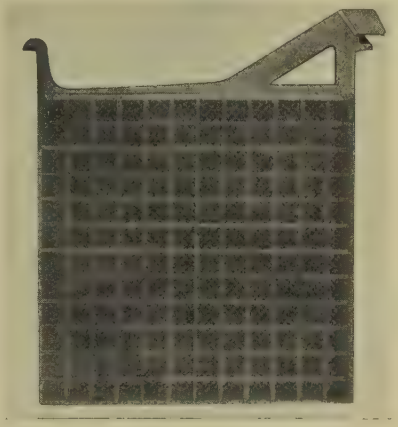

FIG. 20.—Box negative plate.

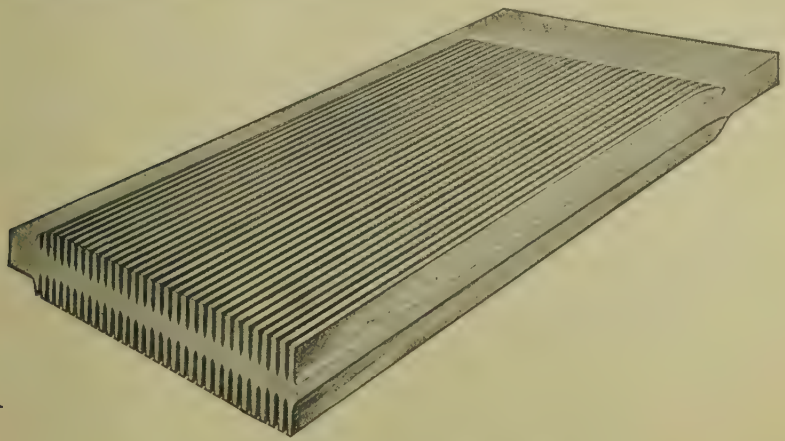

FIG. 21.—Section of a spun plate.

sheathed with vulcanized rubber along the top of the plate. For submarine service the negative plate is sheathed at the bottom also.

The box negative plate shown in Fig. 20 is used extensively in stationary batteries. This plate consists of a grid which is cast in

two halves upon perforated lead sheets. The active material for the plate is placed in the boxes of one half, the other half is then placed on top, and the two riveted together.

Of the Planté plates the ordinary type consists of a center web with protruding leaves which have been formed by any one of the processes described on page 32. The C.P., or chemically pure, positive plate (Fig. 21) is made by the spinning process, but its name refers primarily to the method of its formation. This plate is called "chemically pure" because it has been formed in a solution without the addition of the so-called forming agents, such as nitric acid. The C.P. plate differs from other Planté plates in the fact that the active material consists of a rather thin layer of porous crystalline lead peroxide. (Fig. 22). A space is thus provided between the leaves of the plate, which allows for the expansion of the active material during discharge without straining the plate and thereby causing distortion. The electrolyte has free access to the active material over the entire surface of the plate.

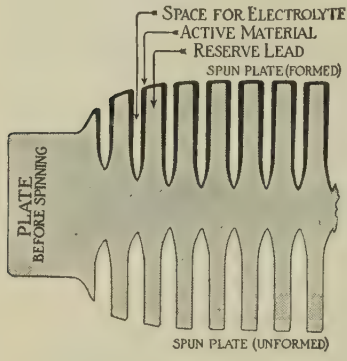

FIG. 22.—Cross-section of a spun plate.

A third type of Planté plate is the Manchester positive (Fig. 23), which consists of buttons of soft lead ribbon which are pressed into a cast grid of the lead-antimony alloy and then formed as a Planté plate. The Tudor positive is a well-known ribbed type of Planté plate which is cast in the cellular form in which it is found in actual use. The Tudor positive is shown in Fig. 24.

Plates for countercells consist of unformed grids or sheets of lead for which the capacity is a minimum. These cells are used entirely for regulating purposes and they develop a potential which is fixed by the line current, but it is not desired that they possess any appreciable capacity. The operation of countercells is described in Chapter VI.

Although a great many different sizes and kinds of plates for lead batteries have been made from time to time, certain sizes have come into common use, and it is therefore worth while to give a table indicating the most common sizes for different types of service and the nominal capacity per positive plate of cells containing them. In the case of plates for stationary batteries, it will be noticed that there is a simple relation between the capacity of the various sizes, which is hardly sug-

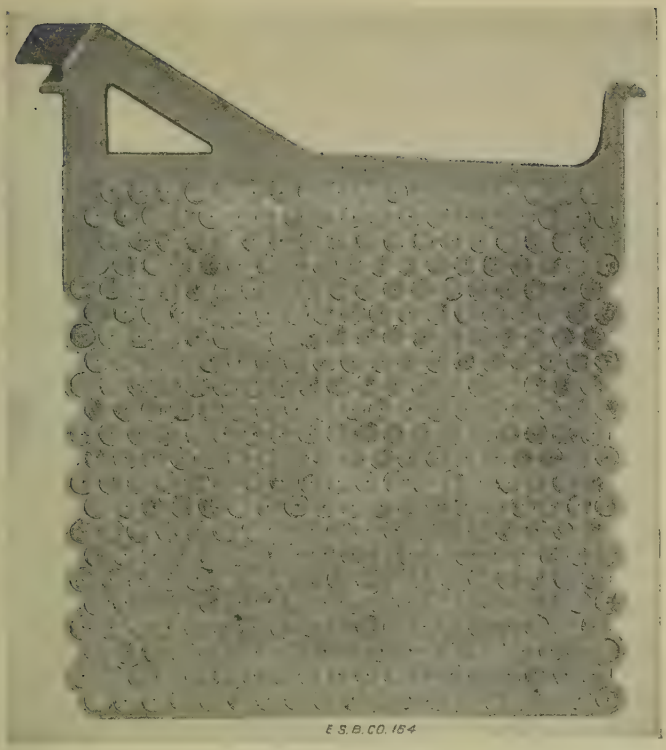

FIG. 23.—Manchester positive plate.

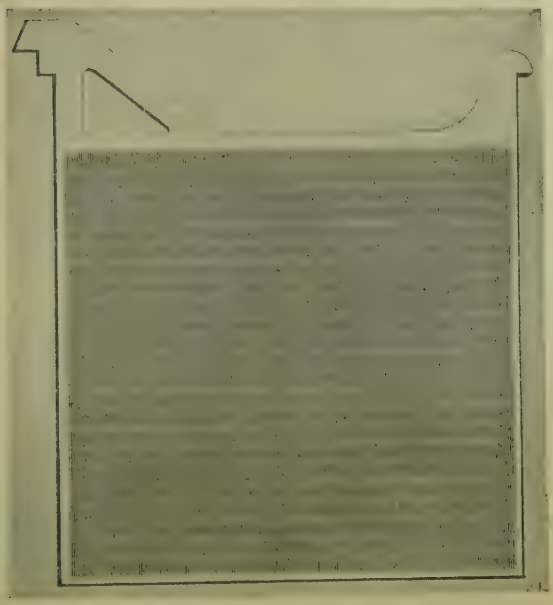

FIG. 24.—Tudor positive plate.

gested by the irregularity of the dimensions. In making use of this table it should be remembered that the list of sizes is by no means complete and that the capacity will vary somewhat with the quality and thickness of the plates. The figures which are given here serve as a general guide to the size and performance of these plates.

TABLE VIII

PLATE SIZES, LEAD BATTERIES

The sizes listed are those most commonly used, but there are variations in dimensions and capacity. The capacities are calculated from the rated capacities of ordinary types.

	Width, Inches	Height, Inches	Nominal Capacity per Positive Plate, Ampere-hours	Rate of Discharge, Hours
Starting and lighting	$5\frac{5}{8}$	$4\frac{3}{4}$	13	5
" " "	$5\frac{5}{8}$	$5\frac{1}{4}$	15	5
Isolated plant	$5\frac{13}{16}$	$5\frac{7}{8}$	22	8
" "	$7\frac{3}{4}$	$7\frac{3}{4}$	40	8 (Planté plate)
" "	$7\frac{3}{4}$	$7\frac{3}{4}$	44	8 (Pasted plate)
Car lighting plates	$7\frac{3}{4}$	$10\frac{1}{2}$	50	8
Vehicle plates	$5\frac{3}{4}$	$8\frac{5}{8}$	28	5
Stationary plates	3	3	5	8
" "	$4\frac{3}{8}$	4	10	8
" "	6	6	20	8
" "	$7\frac{3}{4}$	$7\frac{3}{4}$	40	8
" "	11	$10\frac{1}{2}$	80	8
" "	$15\frac{5}{16}$	$15\frac{5}{16}$	160	8
" "	$15\frac{5}{16}$	$30\frac{3}{4}$	320	8
" "	$18\frac{5}{8}$	$18\frac{5}{8}$	184	8

7. ASSEMBLY OF LEAD-ACID CELLS

The remainder of the process for the manufacture of lead storage batteries deals with problems which are of comparatively little interest to a student. They will, therefore, be described very briefly. The plates, after formation, are assembled into positive and negative groups by burning the plate lugs to the connecting straps or bars (Figs. 25 and 27). The larger sizes of plates, especially those for stationary cells, are burned to heavy cross bars which serve also as the terminal of the cell.

This is usually done at the place where the stationary battery is to be

FIG. 25.—Connecting strap, showing sealing nut.

installed. The positive and negative groups consist of a set of positive or negative plates for each cell. These groups are interleaved, the positive and negative plates alternating. The separators are then placed between the plates of opposite polarity, with the grooved side of the separator next to the positive plate. If rubber separators are used, they are inserted between the positive plates and the wood separators. The assembled positive and negative groups with separators are called the element of the storage cell. After the assembly of the element is complete, it is placed in the jar or container, and the cover of the cell is sealed on. (Fig. 26).

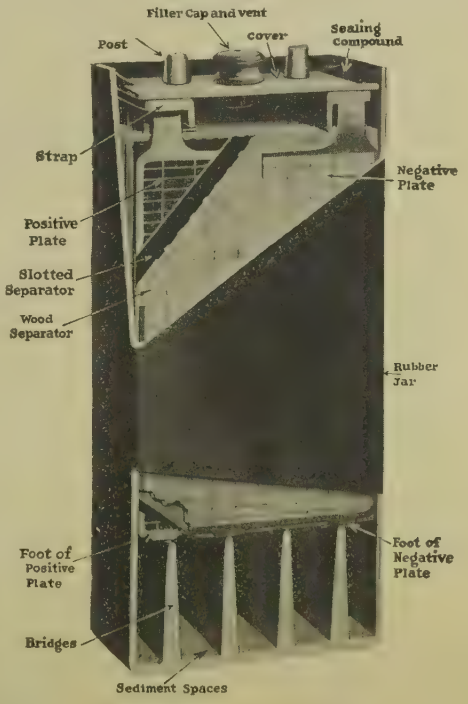

FIG. 26.—A storage cell of the lead-acid type.

Connectors between the individual cells may be of several different kinds. Pure lead connectors are used when high conductivity is required without severe mechanical conditions. The most common type of connector is made from a casting of lead-antimony alloy. These

connectors may be burned to the projecting terminals of the cell and are more durable than the soft lead connectors. Copper connectors with heavy lead plating are sometimes used in batteries for vehicle or locomotive work, since they combine high conductivity with flexibility, the latter property enabling them to absorb the strains that might otherwise crack the jars of the battery. The copper strips usually have a loop in the middle to increase the flexibility and have alloy castings on the ends which may be burned to the terminals of the cell. Intercell connectors are commonly referred to as burned or bolted, these terms indicating whether the connectors are attached to the cell post by the lead-burning process or clamped by a threaded bolt.

FIG. 27.—Assembling a group of plates.

The resistance of the intercell connectors is a matter of considerable importance, since the energy which is wasted in the form of heat in these connectors varies as the square of the current. If the intercell connectors are made very large for the current which the battery is designed to carry, unnecessary material is used and the weight of the battery unduly increased. In Chapter X a discussion of the resistance of the intercell connectors is given for the automobile, vehicle, and airplane types of batteries, for which this is a matter of particular importance.

The individual cells are mounted in boxes, crates, or trays, according to the type of battery and the service for which it is designed. It is unnecessary to discuss them further.

8. HAZARDS IN THE PROCESSES OF MANUFACTURE

The poisonous nature of lead and its compounds gives rise to certain hazards in the processes of manufacture which deserve attention because

of the large increase in the number of small manufacturing plants making batteries for automobile service. In several European countries, governmental regulations are enforced with respect to the conditions of work, and have greatly lessened the number of cases of lead poisoning occurring among the employees. In the United States such regulations are a matter of state law, but a study [28] of the subject has been made by the Federal Bureau of Labor Statistics. Very few of the states have adopted regulations dealing with storage battery factories, but the largest factories are located in states that have regulations.

The sources of the poisoning are primarily the dust of lead and its oxides, and the fumes from the melting pots and lead burning. The compounds of lead are poisonous practically in proportion to their solubility. Bluish fumes may often be observed over the melting pot when the alloy is ladled out or the dross skimmed off. The quantity of these fumes probably depends on the temperature of the molten metal, but they are generally present, and a hood with a forced air suction is necessary. The dross should not be thrown on the floor. The process of burning the plates to the straps and the connectors to the posts gives rise to lead fumes and requires that good ventilation be provided. Some dust arises from trimming the grids and cleaning the lugs, but the greater quantity of dust is due to the oxides of lead used for pasting the plates. The material for the paste must be weighed and mixed dry. This is a dusty process that requires especial attention. It should be carried on in a separate room provided with forced ventilation, and the operatives should wear respirators. There is less danger in the pasting process when the paste is wet, but scraps of paste falling on the table or floor produce dust, so that the pasting room may present a brilliant scarlet or yellow appearance. The latter color is due to the litharge, which does not show as much as the more brilliant red oxide, but is sometimes said to be more dangerous because more dusty. Pasting rooms should always be provided with adequate cleaning facilities and ventilation.

The forming rooms are often filled with fumes that are irritating to the throat of a person not accustomed to them. These fumes are caused by the acid being sprayed into the air by bursting bubbles of gas as they rise to the top of the forming tanks. Although the discomfort is greater in such a room as this, the hazard is less. Medical evidence is conflicting as to the possible bad effects of the fumes. It is, of course, necessary that the ventilation be sufficient to carry off the hydrogen generated, in order to avoid explosions, and the sulphuric acid

[28] Bulletin of the Bureau of Labor Statistics No. 165, "Lead Poisoning in the Manufacture of Storage Batteries," by Alice Hamilton, M.D.

content of the air must be kept low to preserve the insulation as well as to avoid discomfort to the workers.

The larger and more progressive companies making storage batteries have provided the necessary ventilation of various rooms and have also provided washrooms, locker rooms, and in some cases lunch rooms and medical inspection. Sometimes the workmen fail to make intelligent use of the facilities provided and thereby expose themselves to unnecessary risks. In the smaller plants, the different processes are often carried out in the same room, and the natural draft of air through a window depended on for ventilation. Such conditions are not safe or satisfactory.

9. THE EDISON CELL (ALKALINE TYPE)

The alkaline type of storage battery is most familiarly known in this country as the Edison storage cell. Other forms of this cell have, however, been made in European countries; these include the Junger and the Gouin. The general character of the reactions of the plates of these cells is the same, but the construction of the various parts is different. The positive plates are filled with nickelous hydroxide as the active material. After formation this is converted to a higher oxide of nickel. Since this material is a non-conductor, additions of flake nickel or graphite have been made to provide the necessary conductivity. The flake nickel is now used entirely for this purpose in the Edison battery. The active material of the negative plate is finely divided iron. Since the Edison cell is the one of chief importance among the alkaline cells in this country, the following discussion relates primarily to this type.

a. Positive Plates.

A positive plate is shown in Fig. 28.

Preparation of Nickelous Hydroxide.—Metallic nickel in the form of shot is dissolved in sulphuric acid. The hydrogen which is evolved during this process is collected and saved for use in connection with other processes in the manufacture of the cell. Certain impurities, such as copper, zinc, antimony, and iron, are usually present in the solution and must be removed. The solution of nickel sulphate is then sprayed into tanks containing a 10 to 15 per cent solution of hot sodium hydroxide. Nickelous hydroxide is precipitated as a result of the reaction which takes place. The precipitate is collected and dried, but it contains considerable amounts of sodium hydroxide, carbonates, and sulphates. These may be removed by leaching the mass with hot water. The nickelous hydroxide is then dried again and tested to determine its

quality. If it is found to be satisfactory it is ground and sifted, the material used ranging between 30 and 190 mesh.

Preparation of the Flake Nickel.—The flake nickel which is added to the nickelous hydroxide in making the plates is required to give the active material sufficient electrical conductivity. The flake nickel consists of small squares $\frac{1}{16}$ inch on the edge and 0.00004 inch in thickness. It is prepared by an interesting nickel-plating process. Ten revolving copper cylinders are carried by a crane and dipped alternately in copper and nickel-plating baths for sufficient time to deposit the thin layers of metal which are required. The cylinders are washed by sprays of water between each immersion in the plating tank. This process of alternately plating copper and nickel is repeated 125 times so that the sheet of deposited metal on the cylinders consists of 125 layers each of copper and nickel. The time required for this operation is about five hours. The copper-nickel sheet is then stripped from the cylinders and cut into squares $\frac{1}{16}$ inch on the edge. The copper is dissolved chemically, leaving the nickel as thin flakes, each little square yielding 125 of these flakes. The flake nickel is washed and centrifuged and dried over steam coils. In its final state a bushel of the material weighs only $4\frac{1}{2}$ pounds.

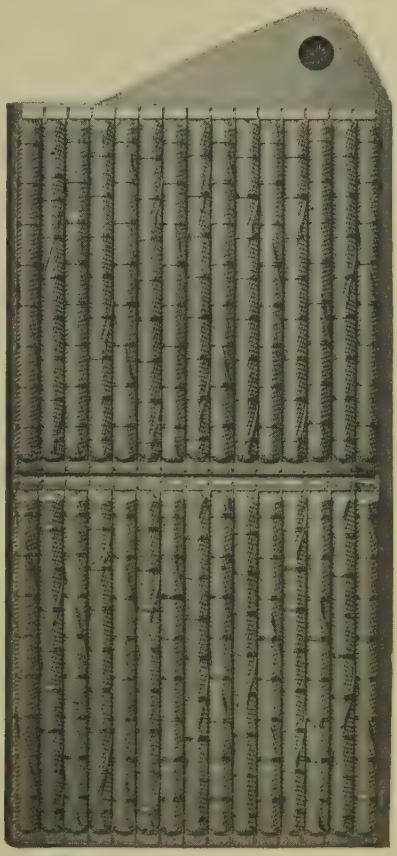

FIG. 28.—Positive plate of the Edison cell, type A.

Tubes to Contain the Active Material.—Since 1908, the active material for the positive plates of the Edison batteries has been contained in steel tubes (Fig. 29). Prior to this time the material was contained in pockets somewhat similar to those which are used for the negative plates. This earlier construction was abandoned because of the strains created by the swelling of the active material. The tubes are prepared from cold-rolled carbon-steel ribbon which is perforated

by passing through special rolls which punch 560 holes to the square inch. The burrs are removed by emery wheels and the ribbon is cleaned by revolving wire brushes, to insure that the perforations are open so that the electrolyte may have free access to the active material of the plate. The steel ribbon is then nickel-plated. This is done as it passes continuously through a series of tanks containing the necessary solutions for cleaning, plating, and washing. The first of these tanks consists of a solution of potassium hydroxide to remove the grease from the steel ribbon. This is followed by a tank of hot water to wash off the alkali. The next tank contains a solution of the double salt, nickel-ammonium sulphate, in which the nickel plating is done. This is followed by two washing tanks containing hot and cold water, and finally the steel ribbon is passed through a tank containing a dilute solution of ammonium

FIG. 29.—Positive tube of Edison cell.

hydroxide to remove any possible trace of acid solution. The time required for a given point on this ribbon to pass through the series of plating and other baths is about eight minutes. After the nickel-plating process is finished, the steel ribbon is dried and annealed in an atmosphere of hydrogen. The purpose of this annealing is to weld together the nickel plate and the underlying steel in order to prevent possible scaling off of the nickel plating. This is done in an atmosphere of hydrogen to prevent the discoloration that might otherwise take place.

The tubes which contain the active material of the positive plates are made from the nickel-plated steel ribbon, by winding them spirally. The seams are lapped and swaged flat. These tubes are made in rights and lefts, which are alternated in the assembly of the plate, thereby equalizing the strains which would tend to cause buckling. The tubes are made $\frac{1}{4}$ or $\frac{3}{16}$ inch in diameter with a standard length of $4\frac{1}{2}$ inches.

Filling the Tubes.—A cap is placed at the bottom of each tube, and a group of tubes are then put into a filling machine which tamps the active material into them. Eight tubes are mounted in molds below a row of weighted ramrods that fall by gravity, striking a blow of 2000 pounds per square inch. The filling machine is provided with two hoppers, one of which dumps a specified charge of nickelous hydroxide into each tube, and the other a certain quantity of the flake nickel.

This is followed by a blow of the ramrod. The process is repeated 315 times, so that there are 630 layers of alternate nickelous hydroxide and flake nickel (Fig. 30). The layer of the nickel is somewhat thinner than the layer of the hydrate, the nickel constituting about 14 per cent of the contents of the tube. After the tubes are completely filled, the ends are pinched shut to form terminals which are suitable for clamping into steel grids. Before being placed in the grids, however, the tubes are reinforced by eight seamless nickel-plated steel rings. These are put on each tube to prevent possible bursting of the tube because of the swelling of the active material which takes place during the forming process. The active material of the positive plate is said to contract somewhat on discharge.

Fig. 30.—Magnified section vertically through a positive tube, showing the alternate layers of nickelous hydroxide and flake nickel.

Positive Grids.—These are steel punchings (Fig. 31) which are nickel-plated and annealed as has been described above. The punched

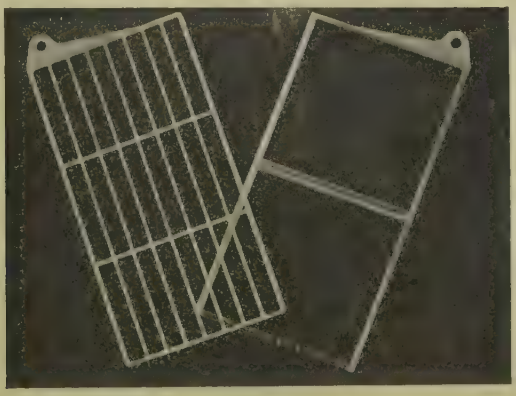

Fig. 31.—Grids of the Edison cell; negative left, positive right.

ends of the tubes are caught underneath ears projecting from the

sides of the plate. The tubes are clamped in place by a hydraulic press.

b. Negative Plates.

A negative plate is shown in Fig. 32.

Active Material.—Pure iron in a finely divided state is treated with sulphuric acid. Hydrogen gas is evolved during this process, and this is saved for other uses in the manufacture of the batteries. The iron, in the form of ferrous sulphate, is recrystallized several times and then centrifuged to free it from mother liquor. It is then dried at a temperature of 200° C. The iron is then roasted in an oxidizing atmosphere to the ferric state (Fe_2O_3). Traces of sulphate in this material are removed by leaching and it is dried and reduced in an atmosphere of hydrogen in a muffle furnace. The material is allowed to cool in an atmosphere of hydrogen and then covered with a solution of sodium hydroxide to prevent oxidation. It is then dried and ground and mixed with 6 per cent of yellow oxide of mercury. The latter serves to increase the conductivity of the mixture and keeps the iron active, overcoming any traces of the ferric oxide.

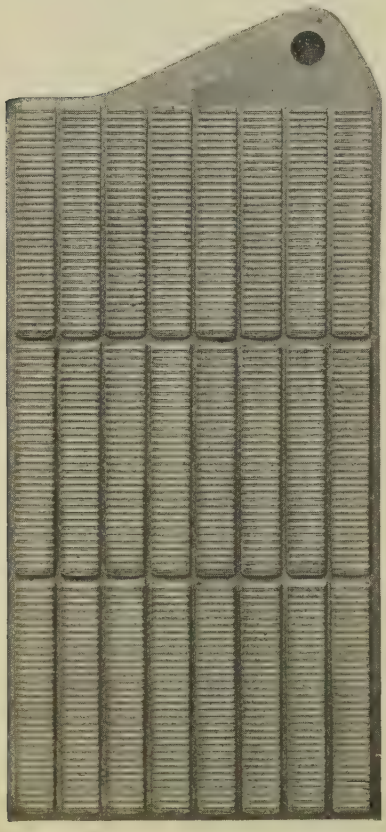

Fig. 32.—Negative plate of the Edison cell, type A.

Negative Pockets.—The active material for the negative plates is contained in steel boxes or pockets (Fig. 33) with perforated sides. These are prepared from the nickel-plated ribbon similar to that used for making positive tubes. The ribbon is cut to the proper length and pressed into a form similar to the two halves of a pasteboard box. These halves are then put together, one end being left open for the filling. The active material is tamped into these pockets as the black oxide of

iron. The pockets are fastened in the negative grid (Fig. 31), which is a nickel-plated steel punching having a series of parallel openings of the proper size to take the pockets of active material. The pockets are put in place under a hydraulic press, which seals the boxes

FIG. 33.—Negative pocket of Edison cell.

and crimps the sides. The pockets are 3 inches long by $\frac{1}{2}$ inch wide and $\frac{1}{8}$ inch thick.

c. Assembly.

The necessary number of plates of each kind for any particular size of cell are mounted on steel rods which pass through the eyes of the grids at the top of the plates. The plates are separated from one another by means of washers fitting on this rod, and are locked in place by a lock washer and nut which is screwed on the end of the rod. Groups of positive and negative plates, corresponding to the positive and negative groups of the lead storage batteries, are formed in this way. The rod which supports the positive or negative plates and connects them electrically is called the " connecting rod." The groups of positive and negative plates are intermeshed to form the element and are separated by hard rubber pins. Side separators, consisting of flat sheets of hard rubber, are used around the outside of the element to insulate it from the walls of the container. The element, when completely assembled, is slipped into the containing jar or can and rests upon a bridge work of hard rubber at the bottom. A complete cell is shown in Fig. 34. The can is made from sheet steel, nickel-plated, with sides corrugated to provide additional strength. It is bent into shape around a form and the side seams are welded by an oxy-acetylene flame. The bottom of the cell is welded to the sides of the can, and after the element is in place the top seams are welded also. The container parts, such as cover, sides, and bottom, are nickel-plated before welding and after welding also. The terminal posts for the plate groups pass through openings in the top of the cell and are sealed into place by a combination of hard and soft rubber gaskets and bushings. The bushing around the positive pole is red, while that around the negative pole is black. In this way a clear indication of the polarity of the cell is given. In the

center of the cover is a combination valve and filler (Fig. 35). This consists of a hemispherical valve equipped with a spring which permits the valve to be opened for filling the cell with electrolyte or water, but normally presses the valve against the seat. As the pressure of gas in the cell rises when it is on charge, the valve is displaced, allowing the gas to escape. This gives rise to the familiar popping sound which is

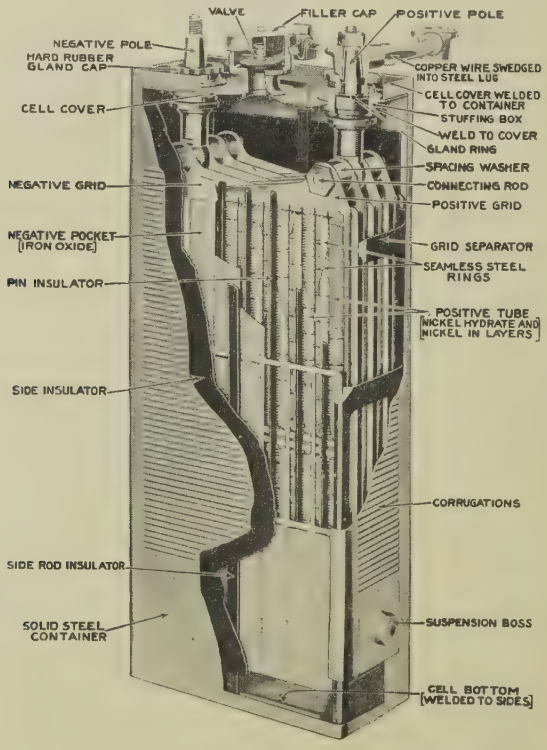

FIG. 34.—The Edison cell, nickel-iron or alkaline type of storage cell.

often heard when batteries of this type are being charged. The satisfactory operation of the cell depends in considerable measure upon the gas valve, since the electrolyte, potassium hydroxide, has a strong tendency to absorb the carbon dioxide from the air. The valves may be easily opened, however, for filling the cells with water.

The terminal posts for the cells are of steel, tapered and ground to fit the lugs of the intercell or intertray connectors. The top of the cell is threaded to take a lock nut. The lugs of the intercell connectors are drop forgings of steel, bored, reamed, and ground to fit the taper of

the terminal posts. Both the terminal posts and the lugs are finished by nickel-plating and annealing in an atmosphere of hydrogen. This prevents the corrosion of the steel and provides a satisfactory contact surface in spite of the thin oxide film that exists on the nickel surfaces. The connecting links are copper swaged into the lugs and the whole nickel-plated. The lugs may easily be removed from the terminal posts by the use of a wrench and jack; these tools are necessary because the lug generally becomes " frozen " to the posts.

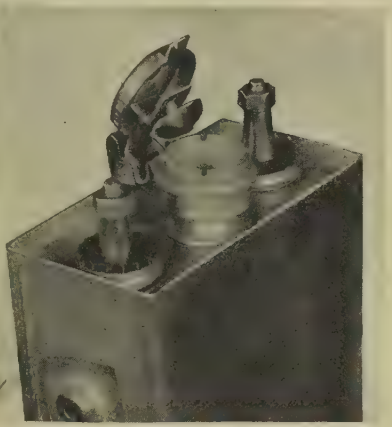

FIG. 35.—Gas valve and vent on the Edison cell.

d. Electrolyte.

The electrolyte for the alkaline cells is a solution of potassium hydroxide in water. For the Edison cells a small amount of lithium hydroxide is added because of its beneficial effect on the capacity of the cells. As a substitute for the potassium hydroxide, an electrolyte of sodium hydroxide has been used, but the physical properties of this solution are not as good for the purpose as those of the potassium solution. The preparation of the electrolyte and the physical properties of it are described in Chapter III.

FIG. 36.—Method of supporting Edison cells in the tray.

e. Trays.

The cells are mounted in trays which have open sides and in some cases are bottomless. The cells are supported in these trays by bosses (Fig. 36) on the sides of the cans of the individual cells that fit into rubber buttons in the sides of the tray. These supports serve also to separate and insulate the cells, which is quite necessary because the containers for these cells are metallic conductors.

f. Table of Plate Sizes.

The sizes of the Edison batteries are described in Chapter X in connection with the different applications which are made of them. In this place, however, will be given a table analogous to that which has been given for the lead batteries, showing the different types of plates for Edison storage batteries, the number of tubes and pockets that they contain, with dimensions, and the nominal capacity of these plates at the five-hour rate of discharge. The nomenclature for the Edison cells is simple. The type of cell is designated by a letter followed by a number. The letter indicates the type of plate which the cell contains, and the number indicates the number of positive plates. This system of designation differs from that of the lead batteries, since only the number of positive plates is indicated. Lead batteries, on the other hand, are designated as 11, 15, etc., plates, by which is meant the total number of plates both positive and negative within the cell. An exception to the above rule in the case of the Edison batteries is made for the smaller sizes; for these the number indicates the number of positive tubes instead of the number of positive plates.

The standard plate for the Edison battery is called the " A " plate. This is designed for general purposes, electric vehicles, trucks, locomotives, isolated farm lighting plants, and railway train lighting. The next most common plate is known as the " B " plate. This is a plate of half the capacity of the " A " type. It is used for lighting service on automobiles and launches, ignition, fire- and burglar-alarm systems, and clocks. The " G " plate contains positive tubes of $\frac{3}{16}$-inch diameter instead of the more usual $\frac{1}{4}$-inch tubes, and is designed especially for service on electric locomotives which require a battery of small internal resistance because of the heavy demands made upon the battery for current. The " G " type plate was designed to act similarly to the thin plates used in lead batteries and it has some of the same disadvantages, such as shorter life than the standard " A " plate. The " L " type cells are used in hand lanterns. The " M " type of battery contains positive plates having tubes $3\frac{1}{8}$ inches long and seven tubes to the plate. These are small cells designed for use with mine lamps, clock circuits, and time recorders. The " W " type of cell is the smallest form made. It is designed for work in which potential rather than current is required. A familiar example of this use is in radio service. In some cases two " W " cells are welded together, forming a so-called twinned cell for which the voltage is double that of a single cell. In addition to the types named above, there is also the " J " type, but this has no present use.

TABLE IX

Types of Edison Storage Battery Plates

The types of plates are designated by letters; the types of cells by letters and numbers, the former indicating the type of plate and the latter the number of positive plates in the cell, except in case of the smaller sizes, Types M, L, and W.

Type of Plate	Number of Tubes per Positive Plate	Dimensions of Tubes		Number of Pockets per Negative Plate	Dimensions of Pockets			Nominal Capacity per Positive Plate, 5-hour Rate, Ampere-hour
		Diameter, Inch	Length, Inches		Length, Inches	Width, Inch	Thickness, Inch	
A	30	$\frac{1}{4}$	$4\frac{1}{2}$	24	3	$\frac{1}{2}$	$\frac{1}{8}$	37.5
B	15	$\frac{1}{4}$	$4\frac{1}{2}$	16	$2\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{8}$	18.75
G	40	$\frac{3}{16}$	$4\frac{1}{2}$	24	3	$\frac{1}{2}$	$\frac{1}{8}$	25.0
J	20	$\frac{3}{16}$	$4\frac{1}{2}$	16	$2\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{8}$	12.5
M	4 or 7	$\frac{1}{4}$	$3\frac{1}{8}$	2 or 5	$2\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{8}$	2.25 or 5.62
L	10*	$\frac{3}{16}$	$4\frac{1}{2}$	8	$2\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{8}$	6.25
W	3†	$\frac{1}{4}$ and $\frac{3}{16}$	$4\frac{1}{2}$	2	$2\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{8}$	3.12

* The number for types M and L, indicate the number of positive tubes in the battery instead of the number of positive plates.

† The W2A cell has a positive plate consisting of two $\frac{1}{4}$ inch tubes and one $\frac{3}{16}$ inch tube.

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CHAPTER III

THE ELECTROLYTE

The electrolyte for lead storage batteries is a solution of sulphuric acid. This has been used since the beginning of the industry, but at various times the addition of certain substances has been suggested. Some of these have proved harmful, others are of doubtful value although harmless. With the greatly increased demand for storage batteries by non-technical users, because of the adoption of the batteries for starting and lighting service on automobiles, there have recently appeared a number of so-called special electrolytes which are sold with extravagant claims. The use of these electrolytes cannot be recommended. In this chapter a brief description of the preparation of sulphuric acid and the physical and chemical properties of its solutions, which are of importance in studying the general subject of storage batteries, will be given.

Sulphuric acid is one of the most important of chemical compounds because of the great variety of its uses. Its manufacture antedates the beginnings of modern chemistry. It is marketed under a variety of names, depending on the strength and purity of the acid. *Chamber acid* is a dilute acid containing from 62 to 70 per cent sulphuric acid; *tower acid* contains 75 to 82 per cent acid; *oil of vitriol* contains 93 to 97 per cent acid; *monohydrate* contains about 98.5 per cent acid and is the strongest acid that can be prepared by evaporation; *fuming acid*, or *oleum*, contains sulphur trioxide dissolved in concentrated sulphuric acid. The significance of these names will appear in later sections. For the storage battery, the chemically pure oil of vitriol, diluted to the proper concentration, is of greatest importance. Since the term "oil of vitriol" is often used to designate the more impure or technical grade of acid, including the brown oil of vitriol, it is better to adhere to the term "sulphuric acid," meaning thereby the chemically pure acid. The amount of this concentrated acid used per year in this country for storage-battery purposes is probably in excess of 30,000,000 pounds.

1. THE PRODUCTION OF SULPHURIC ACID

Sulphuric acid in the free state occurs in small quantities in volcanic regions, and natural sulphates are abundant; but these sources are not

utilized for producing the acid in large quantities. The commercial processes are based on the oxidation of sulphur dioxide to the trioxide state, which in combination with water yields sulphuric acid.

The combustion of sulphur in the air results in the formation of sulphur dioxide, SO_2, which is a colorless gas having a suffocating odor. This dioxide is not combustible, but may be further oxidized to sulphur trioxide, SO_3, through the agency of nitrogen oxides or in the presence of certain catalysts. The trioxide of sulphur is also called sulphuric anhydride. It is a transparent crystalline solid that unites with water, with explosive violence, and with the evolution of a large amount of heat, forming sulphuric acid. The general reaction may be represented by the following equation:

$$SO_2+O+H_2O=H_2SO_4$$

This reaction, however, is not as simple as the equation would indicate. The oxidation of the dioxide to the trioxide state is a slow reaction that is difficult to perform, and the sulphuric anhydride forms, with the water, a series of compounds that are called hydrates. These may be represented by the formula $m\cdot SO_3\cdot n\cdot H_2O$ in which m and n are whole numbers indicating the number of gram-molecules of the anhydride and water respectively. If m is less than n or equal to it, the acid is of the ordinary non-fuming variety. When m exceeds n, the formula represents fuming sulphuric acid. This fact enables us to distinguish the fuming from the non-fuming acid by the percentage content of the sulphuric anhydride. One gram-molecule of the anhydride weighs 80.06 grams, and a gram-molecule of water weighs 18.016 grams. The limiting percentage of the anhydride in the non-fuming acid is, therefore, the ratio of 80.06 to 98.076 which equals 81.63 per cent.

Since 98.076 is the molecular weight of sulphuric acid, according to the formula H_2SO_4 it is possible to compute from the limiting percentage of the anhydride the amount of it present in any solution when the percentage of sulphuric acid is known. For example: The acid of specific gravity 1.300, commonly used in certain types of batteries, contains 39.1 per cent of sulphuric acid and $39.1\times0.8163=31.9$ per cent of the sulphuric anhydride.

Two processes are used at the present time for the manufacture of sulphuric acid. These are commonly called the "chamber" and the "contact" processes. The difference between them consists in the method employed to oxidize the sulphur dioxide to the trioxide state. The contact process is supplanting the chamber process for the preparation of concentrated acid, but two-thirds of the sulphuric acid produced in the United States is made by the chamber process.

As a preliminary to either of these processes, the production of sulphur dioxide is necessary. The purest sulphur dioxide is produced by the direct combustion of sulphur, but a common method is by the roasting of iron pyrites, which contain ordinarily from 40 to 50 per cent of sulphur. Other raw materials include zinc blende, galena, and the spent oxides of gas works. The oxide obtained by burning pure sulphur is free from arsenic, iron, copper, and zinc, which usually appear in the gas obtained by roasting the pyrites.

In the chamber process, the oxidation of the sulphur dioxide is effected by the aid of oxides of nitrogen in a series of lead-lined chambers, from which the process takes its name. The hot gases from the sulphur burners or the roasting ovens pass into a tower, called the Glover tower, filled with broken fire-brick over which flows a stream of dilute sulphuric acid (part of the acid from the chambers), which cools the gases and effects a partial concentration of acid. Concentrated sulphuric acid, containing oxides of nitrogen, also flows in this tower. The oxides of nitrogen are liberated near the top of the tower by the dilution of the strong acid by the weak acid. The oxides of nitrogen and sulphur mix, starting the formation of the sulphur trioxide, which process is continued in the chambers to which the mixed gases next pass. Water and nitric acid are sprayed into these chambers. The former absorbs the trioxide as it forms. The oxides of nitrogen pass on to the Gay-Lussac tower, where they are reabsorbed by concentrated sulphuric acid and are used again. The principal product of the plant is the chamber acid drawn from the chambers. As this is relatively dilute it is concentrated by evaporation. Platinum, iron, silica, and glass serve as materials for the concentrating apparatus. These materials are not entirely inert. About one gram of platinum is lost per ton of acid that is concentrated in platinum stills or dishes. This represents about one part of platinum in one million parts of the acid, which would be sufficient to cause trouble in a storage battery. Platinum has become so expensive that it is rarely used now for this purpose.

The contact process is simpler. Sulphur dioxide may be oxidized to the trioxide state in the presence of sponge platinum and certain other catalysts, at a temperature of about 400° to 450° C. The process will proceed with evolution of much heat after being started. Other catalysts that are sometimes employed for this purpose are iron oxide, copper oxide, oxides of manganese, and a number of others. Platinum, however, is usually employed and may be used at a lower temperature. The combination of pure water and pure sulphur trioxide results in the formation of pure sulphuric acid, which may be made of any desired degree of concentration. The contact process also requires two stages

for the formation of sulphuric acid. These may be represented by the following formulas:

$$\left\{\begin{array}{l} SO_2+O = SO_3 \\ SO_3+H_2O=H_2SO_4 \end{array}\right\} \quad \text{and}$$

Impurities, such as arsenic from the pyrite, must be removed, as they interfere with the action of the catalysts.

Storage batteries require the highest purity of sulphuric acid. For this reason acid made from pure sulphur is preferable to acid made from pyrites. The source of the acid cannot always be ascertained, and it is important, therefore, to have specifications (page 120) to insure an adequate degree of purity.

The conditions for storing and shipping sulphuric acid vary with the concentration. Acid up to about 75 per cent has little effect on lead; above this strength the acid attacks lead if hot. Concentrated acid readily dissolves lead at about 250° C. Monohydrate and fuming acid attack lead at ordinary temperatures. Strong acid, particularly the concentrated acid, has very little effect on iron. Cast iron is somewhat more resistant than wrought iron, except that the former is not suitable for use with fuming acid. Alloys of iron and silicon are very resistant to the non-fuming acid and are extensively used for concentrating the acid up to 98 per cent. Dilute acid cannot be stored in iron containers, and glass carboys or lead-lined tanks are generally used for this purpose.

2. PROPERTIES OF SULPHURIC-ACID SOLUTIONS

Concentrated sulphuric acid is a clear, colorless, and odorless liquid having the consistency of a light oil. Its specific gravity is 1.84 at 15° C. (59° F.) and it contains about 95 per cent acid. It is miscible in all proportions with water, forming a series of hydrates, several of which are of interest in battery investigations. When the acid is mixed with water a large amount of heat is evolved. Its affinity for water is so great that it can extract the elements, oxygen and hydrogen, to form water from some organic substances, such as the wood used for separators in storage batteries. Wood becomes charred if immersed in moderately strong acid. The acid extracts the oxygen and hydrogen from the wood, leaving the carbon which gives the wood a darkened appearance. The concentrated acid boils at 338° C. (640° F.). When it is heated it liberates sulphuric anhydride in the form of a gas, which appears as a dense white vapor because of the absorption of water-vapor from the air.

a. Heat of Dilution.

The amount of heat which is liberated when one gram-molecule of acid is diluted with n gram-molecules of water is shown in the following table. When the amount of water added is so great that the solution may be considered to be infinitely dilute, the total heat evolved is found to be 17.86 kilogram-calories. In Table X, the difference between amounts of heat liberated at any two different concentrations represents the amount of heat that would be liberated in diluting the more concentrated to the less concentrated solution. For example: By diluting $H_2SO_4 \cdot 3H_2O$ to $H_2SO_4 \cdot 99H_2O$, the amount of heat evolved is $16.86 - 11.14 = 5.72$ kilogram-calories. The kilogram-calorie is the amount of heat required to raise the temperature of one kilogram (2.2 pounds) of water one degree Centigrade, the initial temperature being 15° C.

TABLE X

HEAT OF DILUTION AND SPECIFIC HEAT OF SOLUTIONS OF SULPHURIC ACID

(One gram-molecule of acid is diluted with n gram-molecules of water. The heat of dilution is expressed as kilogram-calories.)

Values of n	Per Cent of Acid	Specific Gravity 15°	Heat of Dilution *	Specific Heat †
....	96.0	1.842	.....	0.33
1	84.4	1.779	6.38	0.38
2	73.0	1.651	9.42	0.43
3	64.4	1.551	11.14	0.48
5	52.1	1.421	13.11	0.57
9	37.7	1.288	14.95	0.71
19	22.3	1.161	16.26	0.82
49	10.0	1.069	16.68	0.91
99	5.2	1.035	16.86	0.95
199	2.6	1.018	17.06	0.97
399	1.3	1.009	17.31	0.99
1599	0.3	.....	17.86	....

* Smithsonian Tables, 7th ed., p. 246, 1920.

† Calculated from results of Bode, Zeit. f. Ang. Chem., 2, p. 244, 1889.

The heat of dilution of sulphuric acid is of importance in the theory of storage batteries because of the relation that exists between the voltage and the concentration of the acid. In Chapter IV it will be shown that the voltage of a lead storage cell varies in a definite way with the concentration of the acid in the pores of the plates. It is possible to

calculate, as Dolezalek [1] has done, the voltage corresponding to various concentrations of electrolyte, by an application of the laws of thermodynamics, and by using the heat of dilution for which values are given in the table.

Although the amount of heat evolved when the acid is diluted with a given portion of water is accurately known, the temperature to which the mixture will rise cannot be definitely stated. The temperature will depend on the specific heat of the liquid and the radiation of heat from the solution. When a large amount of acid is prepared for use in storage batteries by dilution in a lead-lined tank, the radiation of heat is proportionately less than when smaller amounts are mixed in containers having less heat insulation. In any case, if it be assumed that the radiation of heat is negligible, it is possible to compute the maximum temperature to which the solution will rise from the heat evolved and the specific heat. For example: If 1 gram-molecule of acid (98 g.) is mixed with 9 gram-molecules of water (162 g.), the initial temperature being 15° C., the temperature rise (neglecting radiation) will be

$$(t^\circ - 15^\circ) = \frac{14{,}950 \text{ cals.}}{0.71 \times 260} = 81^\circ$$

whence $t^\circ = 81^\circ + 15^\circ = 96^\circ$. By experiment with a glass beaker wrapped in a towel, the maximum temperature attained was 85°.

Storage-battery electrolyte is sometimes prepared from the acid of 1.400 sp. gr. In such a case the heat of dilution is $14.95 - 13.11 = 1.84$ kilogram-calories, which is only 12 per cent of the heat evoloved if electrolyte of 1.288 sp. gr. is prepared from the concentrated acid.

b. Contraction of the Solution.

When one volume of sulphuric acid is diluted with one volume of water, the volume of the solution is not two volumes, but slightly less after the solution has cooled to the initial temperature. So it is, also, for any proportions of the acid and water; the sum of the original volumes exceeds the volume of the solution. The contraction is greatest for solutions having a specific gravity of 1.600. Table XI shows the contraction of solutions of various concentrations.

It is often convenient to dilute the sulphuric acid by measured volumes to obtain a required percentage strength or specific gravity. The contraction of the solution must be allowed for, in estimating the required proportions of acid and water. To facilitate the preparation of

[1] Theory of the Lead Accumulator, p. 61.

such solutions, the percentage content of sulphuric acid solutions by both weight and volume are given in Table XVIII.

TABLE XI

CONTRACTION OF SOLUTIONS OF SULPHURIC ACID

(The contraction is expressed as cubic centimeters per kilogram of the solution, 18° C.).

Specific Gravity	Contraction *	Specific Gravity	Contraction *
1.000	0	1.500	60
1.100	25	1.600	62
1.200	42	1.700	60
1.300	51	1.800	48
1.400	57		

* Calculated from Pickering's results, J. Chem. Soc., 57, p. 148, 1890.

To illustrate the application of Tables XI and XVIII to the preparation of electrolytes of various concentrations for storage batteries, the following example is given: Required the per cent of sulphuric acid by volume in a solution of 39.2 per cent by weight (1.300 sp. gr.). One liter of the concentrated acid weighs 1840 grams, whence $\frac{1840}{0.392}=4695$, the total weight of the solution containing 1840 grams of acid. Subtracting from this the weight of the acid, the weight of water is found to be 2855 grams. Since the specific gravity of the water is unity by definition, the sum of the volumes is $2855+1000=3855$ cc. The percentage of acid by volume on this basis would be $\frac{1000}{3855}=25.9$ per cent, which is not the correct result. Table XI shows the contraction to be $51\times4.695=239$ cc. The true volume of the mixture is, therefore, $3855-239=3616$ cc. and the true percentage of acid by volume is $\frac{1000}{3616}=27.6$ per cent, as shown in table XVIII.

c. Resistivity.

The resistance to the passage of an electric current through the electrolyte varies with the concentration and the temperature. The resistivity is a property of the substance itself. It is the resistance of a specimen one centimeter in length and one square centimeter in cross-section. The relation $R=\rho\frac{l}{s}$, where R is the resistance, ρ the resistivity,

l the length, and s the cross-section, indicates the unit for measuring the resistivity. This may be written $\rho = R\frac{s}{l}$. Since the area s has the dimensions of length squared, the dimensional formula for resistivity is the product of a resistance and a length. The unit of resistivity is, therefore, the " ohm-centimeter." It is sometimes spoken of as " ohms per centimeter cube."

The electrolytes used in storage batteries are within the range of minimum resistivities of sulphuric-acid solutions. The lowest resistivity

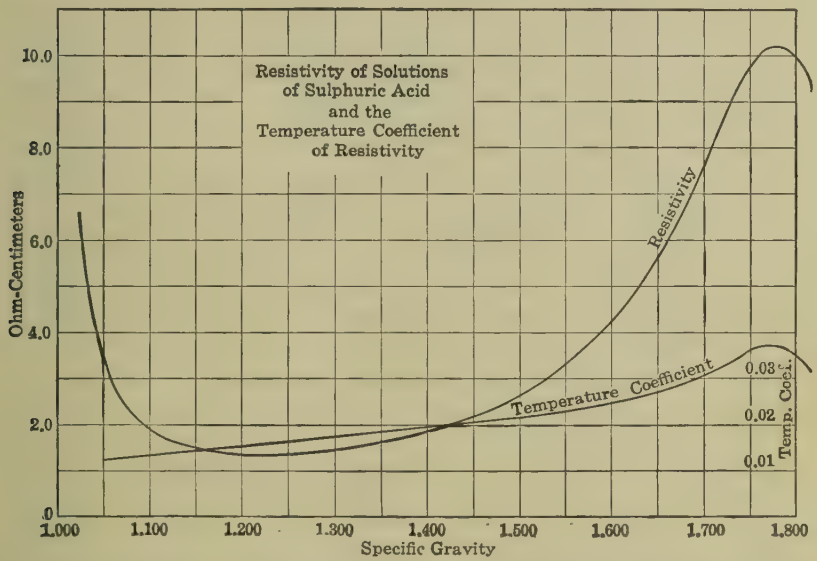

FIG. 37.—Resistivity and temperature coefficient of sulphuric acid solutions.

is for solutions of 1.220 sp. gr., but the values for concentrations between 1.150 and 1.300 do not differ much, as will be seen in Fig. 37. The values of the resistivity for solutions of differing concentration are given in Table XII.

The resistivity of a solution at a temperature differing from 18° may be calculated by the equation:

$$\rho_t = \rho_{18}[1-\alpha(t-18°)]$$

in which α is the temperature coefficient. This is not strictly a constant quantity, since it varies with the concentration. The values of this coefficient are shown in Table XII. At 1.175 sp. gr. the value of α is 0.015, and at 1.300 sp. gr. it is 0.0177. Values between these limits can be obtained by interpolation, assuming the relation to be linear.

TABLE XII

RESISTIVITY OF SOLUTIONS OF SULPHURIC ACID

(Resistivity is expressed in ohm-centimeters for solutions at 18° C.)

Specific Gravity	Resistivity *	Temperature Coefficient of Resistivity	Specific Gravity	Resistivity *	Temperature Coefficient of Resistivity
1.050	3.46	0.0124	1.450	2.18	0.0202
1.100	1.90	0.0136	1.500	2.64	0.021
1.150	1.50	0.0146	1.550	3.30	0.023
1.200	1.36	0.0158	1.600	4.24	0.025
1.250	1.38	0.0168	1.650	5.58	0.027
1.300	1.46	0.0177	1.700	7.64	0.030
1.350	1.61	0.0186	1.750	9.78	0.036
1.400	1.85	0.0194	1.800	9.96	0.035

* Calculated from results of Kohlrausch, Pogg. Ann. 159, p. 233, 1876.

The resistivity of the electrolyte is one of the most important factors in determining the resistance of a storage cell. Unless the internal resistance of the cell is small, a considerable portion of the useful energy of the cell is expended within the cell itself.

d. Freezing Points.

The freezing point of the electrolyte varies with its concentration. It is, therefore, often said to vary with the state of charge of the battery. The importance of knowing the freezing points has increased during the last few years, because of the use of storage batteries on automobiles and aeroplanes, which are often subjected to low temperatures in cold climates and at high altitudes. The freezing points of sulphuric-acid solutions were carefully determined many years ago by Pickering.[2] On page 338 of his paper, the whole freezing-point curve from dilute to concentrated solutions is given. There are several maxima and minima in the curve, owing to the hydrates of sulphur trioxide that are formed at the different concentrations.

In Table XIII the freezing points of solutions corresponding to the specific gravities of the first column are given. These values are in accord with the values adopted as standard by the Manufacturing Chemists' Association in this country. The specific gravities are for the solutions at 15° C. and not at the freezing point. For certain concentrations, a considerable error may be made in estimating the freezing point if allowance is not made for the change in specific gravity at the low

[2] J. Chem. Soc., 57, p. 331, 1890.

temperatures. The temperature coefficient of specific gravity for both the Centigrade and Fahrenheit scales, for all concentrations of electrolyte, is given in Table XVIII.

TABLE XIII

FREEZING POINTS OF SOLUTIONS OF PURE SULPHURIC ACID

Specific Gravity 15° C.	Freezing Points		Specific Gravity 15° C.	Freezing Points	
	Centigrade	Fahrenheit		Centigrade	Fahrenheit
1.000	0	+32	1.450	−29	−20
1.050	− 3.2	+26	1.500	−29	−20
1.100	− 7.7	+18	1.550	−38	−36
1.150	−15	+ 5	1.600	*	*
1.200	−27	−17	1.650	*	*
1.250	−52	−61	1.700	−14	+ 6
1.300	−70	−95	1.750	+ 5	+40
1.350	−49	−56	1.800	+ 5	+42
1.400	−36	−33	1.835	−34	−29

* Freezing points indeterminate.

The freezing points of solutions of pure sulphuric acid are not exactly the same as the freezing points of electrolyte of the same specific gravity taken from storage batteries. The difference is small. For electrolytes of less than 1.290 sp. gr. the freezing points are slightly higher, and for greater specific gravities the freezing points are lower than for solutions of pure acid. Figure 38 shows the freezing point curves of both the pure acid solutions and the battery electrolyte. The reason for the difference probably lies in the slight amount of lead sulphate present in the solution.

In Fig. 38 there are also shown a series of curves in which the specific gravities of solutions are plotted at each ten degrees between 0° and 60° C. and extrapolated below 0° until they intersect the freezing-point curve. These curves were chosen so that specific gravities of 1.200, 1.225, 1.250, etc., fall on the 25° line. By means of this diagram, the freezing point of any electrolyte may be estimated with reasonable accuracy if the specific gravity and temperature are known. For example: The electrolyte in a battery at −20° C. (−4° F.) is found to be 1.256 sp. gr. This point is located on the diagram, and the nearest oblique line is followed to its intersection with the freezing-point curve of the electrolyte, for which the ordinate is −38° C. (−36° F.). The

temperature can, therefore, fall 18° C. (32° F.) before the electrolyte will begin to freeze.

The lowest freezing point is for solutions having a specific gravity of 1.290. When solutions of lower specific gravity than this freeze, crystals of ordinary ice separate from the solution; for higher specific gravities the crystals are of the tetrahydrate of the acid. Since the lowest freezing points are for concentrations of acid corresponding to the electrolyte of automobile batteries when fully charged, it is apparent that there is no danger of such a battery freezing even under the most

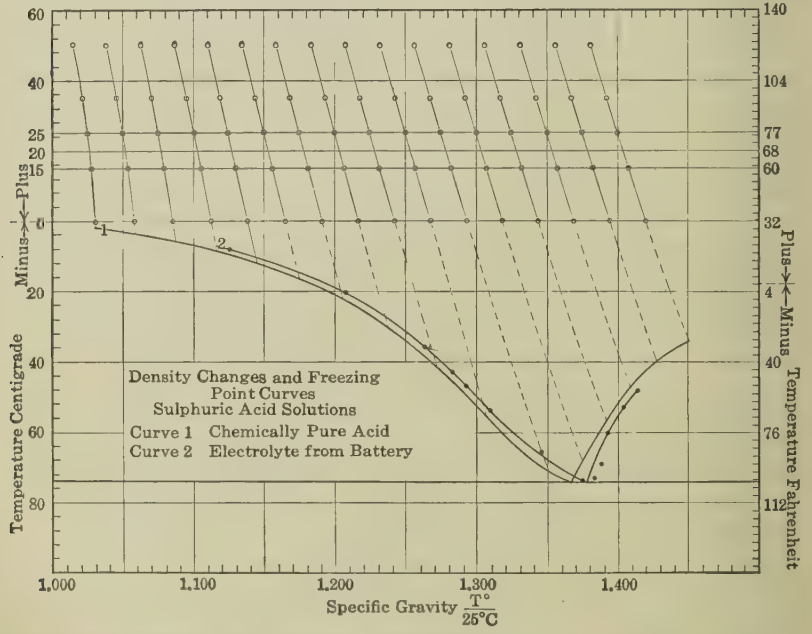

FIG. 38.—Freezing point curve for electrolyte and solutions of sulphuric acid.

severe conditions. If the battery is discharged, however, it will freeze at about −10° C. (+14° F.) or even higher. Electrolyte, or acid for preparing it, should be of the proper specific gravity when stored under severe conditions. Electrolyte of from 1.225 to 1.400 sp. gr. will not freeze under ordinary conditions, but nearly concentrated acid of 1.800 sp. gr. freezes at +5° C. (+41° F.). For concentrated acid the freezing point is much lower. At 1.835 it is −34° C. (−29° F.).

e. Vapor Pressure.

Sulphuric acid is a powerful drying agent. Concentrated acid readily absorbs water vapor from the air in such quantities that a carboy

left unstoppered will soon overflow if nearly filled with acid. Solutions of sulphuric acid have a definite vapor pressure that varies with the concentration and the temperature. The values of the vapor pressure are of theoretical interest in connection with storage batteries, for the same reason as applied to the heat of dilution.

The electrolyte is often said to "evaporate"; most of the water lost from the cells, however, passes off as oxygen and hydrogen during charging. On the other hand, some of the "patent" electrolytes are sold with the claim that they absorb water from the atmosphere. The electrolyte will absorb or give off water vapor according to the relative magnitude of its vapor pressure as compared with that of the surrounding air. If the vapor pressure of the electrolyte exceeds that of the water vapor in the air, evaporation will take place; if it is less, moisture will be absorbed. The simplest method of determining the pressure of water vapor in the air is by some form of dew-point apparatus, or a wet-and-dry bulb hygrometer. The temperatures obtained in such a measurement are referred to suitable tables,[3] in which the corresponding vapor pressures, expressed in millimeters of mercury, are given. For example: On a humid and hot summer day, temperature 95° F. (35° C.) and relative humidity of 87 per cent, the vapor pressure would be 36.7 millimeters; on an average day, temperature 66° F. (19° C.) and relative humidity of 57 per cent, the vapor pressure would be 9.2 millimeters. These values should be compared with the vapor pressures for solutions of sulphuric acid given in Table XIV to determine

TABLE XIV

Vapor Pressure of Solutions of Sulphuric Acid

(The vapor pressures are expressed as millimeters of mercury.)

Specific Gravity	At 15° C., mm.	At 25° C., mm.	At 35° C., mm.
1.000	12.7	23.5	41.8
1.100	12.0	21.7	38.7
1.200	10.2	18.6	33.2
1.300	7.6	14.0	25.0
1.400	4.7	8.6	15.8
1.500	2.3	4.5	8.2
1.600	1.1	2.0	3.5
1.700	0.4	0.6	1.2

[3] Smithsonian Tables, 7th ed., p. 186, is a convenient table for use with a ventilated hygrometer.

whether evaporation or absorption of moisture will take place. Such a comparison shows that the electrolyte of specific gravity 1.300 will absorb water in the first case and evaporate in the second case.

Under ordinary conditions, the vapor pressure of the electrolyte is not very different from that of the water vapor in the air. Stationary batteries, which have electrolyte of low specific gravity and open-top cells, will lose water appreciably by evaporation. Automobile batteries, on the other hand, with a higher specific gravity of electrolyte and closed tops, except for a small vent, will lose very little water by evaporation in the strict sense of the word.

Because of the ability of sulphuric acid to absorb moisture, it is evident that, if spilled, it will remain for long periods of time, or in other words it will not "dry up." This makes it difficult to protect painted surfaces, or other surfaces which are not acid-proof, against corrosion. It is necessary to wash off, or, better still, to neutralize and wash off, any electrolyte which may be spilled or become deposited as a result of gassing upon any surface that is liable to injury.

f. Electrochemical Equivalent.

According to Faraday's law (p. 144) the transformations taking place at the plates of a storage cell are in the proportion of one gram-equivalent of the substance for the passage of 96,500 coulombs of electricity through the cell. This quantity of electricity is sometimes referred to as the electrochemical constant, and it has been named the faraday.

The equation (p. 146) for the reaction within the cell is:

$$PbO_2 + Pb + 2H_2SO_4 \leftrightarrows 2PbSO_4 + 2H_2O$$

It is apparent that for each gram-equivalent of material transformed at the positive and negative plates, two gram-equivalents of acid are decomposed and two gram-equivalents of water are formed during the process of discharge.

Since the gram-molecular weight of sulphuric acid is 98.076 grams and the valence 2, the gram-equivalent weight is 49.038 grams. One ampere-hour may be defined as one ampere flowing continuously for 3600 seconds and is equal, therefore, to 3600 coulombs. The number of ampere-hours in a faraday is readily computed to be 26.80. From these data the number of grams of acid decomposed by the discharge of one ampere-hour is

$$2 \times \frac{49.038}{26.80} = 3.660 \text{ g. acid decomposed.}$$

Similarly, the number of grams of water formed per ampere-hour of discharge may be calculated. The molecular weight of water is 18.016 and its equivalent weight 9.008, whence

$$2\times\frac{9.008}{26.80}=0.672 \text{ g. water formed.}$$

In estimating the quantity of acid taking part in any reaction, it is necessary to draw a sharp distinction between the total quantity of acid reacting and the changes in weight taking place in the electrolyte as represented by the change in specific gravity. The latter are proportional to the equivalents of sulphur trioxide, SO_3, and not to the sulphuric acid, H_2SO_4. The reason for this is made apparent by the equation for the reaction given above. Since the decomposition of two equivalents of acid is accompanied by the formation of two equivalents of water, the net change for the passage of one faraday of electricity during discharge is a loss in weight corresponding to the sulphur trioxide, which may be expressed in grams as follows:

$$\underset{H_2SO_4}{-98.076}+\underset{H_2O}{18.016}=\underset{SO_3}{-80.060} \text{ g.}$$

The minus sign signifies the loss in weight which is manifested in the operation of the cell by the decrease in specific gravity of the electrolyte when discharge takes place. The change in sulphur trioxide content per ampere-hour is

$$2\times\frac{40.030}{26.80}=2.987 \text{ g.}$$

When either charge or discharge takes place, there is a change in volume of the electrolyte as well as a change in the weight. In order to make the process clear, it will be well to take an example, solving it completely:

Example.—A large stationary cell has a capacity of 4000 ampere-hours at the 8-hour rate of discharge. It contains 618 pounds of electrolyte of specific gravity 1.210 at 25° C. when fully charged. Compute the changes in weight and volume and specific gravity of the electrolyte when 4000 ampere-hours are discharged.

In solving this example, it is convenient to convert the weight of electrolyte to the metric system, as this simplifies the later calculations. 618 pounds = 280.3 kilograms. Table XVIII (p. 94) shows that this electrolyte contains 28.9 per cent by weight of H_2SO_4. The amounts of acid and water initially present are, therefore,

$$280.3\times\ 0.289=\ 81.0 \text{ kg. of acid,}$$

$$280.3-81.0\ \ =199.3 \text{ kg. of water.}$$

When 4000 ampere-hours are discharged, the amount of acid consumed is

$$3.660\times4000=14{,}640 \text{ g.}\quad \text{or}\quad 14.64 \text{ kg.}$$

The amount of water formed at the same time is

$$0.672 \times 4000 = 2688 \text{ g.} \quad \text{or} \quad 2.69 \text{ kg.}$$

Comparing the composition of the electrolyte at the beginning and the end, we have

	At the beginning	At the end
Sulphuric acid	81.0 kg.	66.18 kg.
Water	199.3 "	202.19 "
Total	280.3 kg.	268.35 kg.

The net loss in weight of the electrolyte is therefore 11.95 kilograms. This corresponds to the sulphur trioxide removed, as may readily be seen by multiplying the grams of SO_3 equivalent to the passage of one ampere-hour as given above by the number of ampere-hours.

$$2.987 \times 4000 = 11{,}950 \text{ g.} \quad \text{or} \quad 11.95 \text{ kg.}$$

The next step is to compute the specific gravity of the electrolyte at the end of the discharge.

$$\frac{66.16}{268.35} = 24.6 \text{ percent of acid in electrolyte at end.}$$

Assuming the temperature to be 25°, this corresponds to a specific gravity 1.175 according to Table XVIII (p. 94).

The change in the volume of the electrolyte which accompanies the discharge of this cell is computed from the initial and final weights and specific gravities.

$$\text{Initial volume} = \frac{280.3 \text{ kg.}}{1.210 \text{ sp. gr.}} = 231.7 \text{ liters}$$

$$\text{Final volume} = \frac{268.35 \text{ kg.}}{1.175 \text{ sp. gr.}} = 228.3 \text{ liters.}$$

The decrease in volume is, therefore, 3.4 liters or about 0.85 cc. per ampere-hour.

A table of the ampere-hour equivalents contained in unit volume of solution, for the various concentrations, affords the most convenient means of calculating the changes taking place in the operation of storage cells. This method is more direct than the use of formulas and diagrams which have been previously proposed for this purpose. In Table XV are given the theoretical ampere-hours on the assumption that all of the acid could be utilized. This is an impracticable condition, since only part of the acid can be used, but the use of the table will appear from several examples. It is necessary to allow for the changes in volume of the solution which occur during charging and discharging. This is easy to do, because the increase in volume of the solution during charge and the decrease during discharge is practically 1 cc. per ampere-hour. This quantity varies slightly with the concentration of the electrolyte. It

is a little more than 1 cc. per ampere-hour for acid of 1.300 sp. gr., and about 0.85 for acid of 1.200 sp. gr. For most purposes, however, it is sufficient to assume that it is exactly 1 cc. per ampere-hour.

TABLE XV

ELECTROCHEMICAL EQUIVALENT OF SOLUTIONS OF SULPHURIC ACID

(Theoretical values per liter calculated for solutions at 25° C., assuming complete utilization of the acid in accordance with the reaction of a storage battery.)

Specific Gravity	Ampere-hours per Liter	Specific Gravity	Ampere-hours per Liter
1.040	17	1.220	100
1.060	26	1.240	110
1.080	35	1.260	120
1.100	44	1.280	130
1.120	53	1.300	141
1.140	62	1.320	151
1.160	71	1.340	162
1.180	81	1.360	173
1.200	90		

Examples. 1.—A large stationary cell in a lead-lined tank has a capacity of 4000 ampere-hours at the 8-hour rate of discharge. It contains 618 pounds of electrolyte, specific gravity 1.210 at 25° C. when fully charged. Find the coefficient of utilization of the acid at this rate of discharge.

618 pounds = 280.3 kilograms which, divided by the specific gravity, 1.210, = 231.6 liters. From the table, 1 liter = 95 ampere-hours. $231.6 \times 95 = 22{,}000$, the total number of ampere-hours. $\frac{4000}{22{,}000} = 18.2$ per cent the coefficient of utilization.

2. A cell of the vehicle type, containing 6.75 pounds of electrolyte, 1.280 sp. gr. at 25° C., has a capacity of 220 ampere-hours at the 5-hour rate. What is the coefficient of utilization of the acid? *Answer*, 71 per cent.

3. A storage cell of a tractor battery gave 45 amperes for 5 hours and 42 minutes. The initial specific gravity at 25° C. was 1.269 and the final specific gravity, corrected to 25° after allowing sufficient time for diffusion, was 1.099. How many liters of electrolyte were in the cell?

The total ampere-hours discharged were $45 \times 5.7 = 256.5$. Letting x represent the number of liters initially present, the number of liters after the discharge were $(x - 0.256)$. The ampere-hour equivalent of the electrolyte is, by Table XV,

Initial $124.5x$,

Final $43.5(x - 0.256)$.

Whence

$$124.5x - 43.5(x - 0.256) = 256.5.$$

$x = 3.02$ liters. *Answer.*

4. A locomotive cell which gives 90 amperes for 5 hours contains 15 pounds of electrolyte of specific gravity 1.280 at 25° C. What will be the final specific gravity after a 5-hour discharge, corrected to 25° after allowing sufficient time for diffusion to take place?

15 pounds = 6.80 kilograms of electrolyte, and this divided by the specific gravity, 1.280, = 5.31 liters.

The total ampere-hour equivalent is $5.31 \times 130 = 690$

The ampere-hours delivered are $5 \times 90 = 450$

Subtracting, the ampere-hours remaining are 240

During the discharge the volume of the electrolyte has decreased in volume by 450 cc., so that the final volume of electrolyte is $5.31 - 0.45 = 4.86$ liters.

$$\frac{240}{4.86} = 49.4 \text{ ampere-hours equivalent per liter.}$$

The table shows this to correspond to 1.112 sp. gr. *Answer.*

5. A cell from an automobile starting and lighting battery, containing 580 cc. of electrolyte, is rated to give 40 ampere-hours at the 5-hour rate. It is required that the specific gravity at the end of a full discharge shall not fall below 1.140 at 25° C. What must the specific gravity be at the beginning of the discharge?

Since the initial volume is 580 cc., the final volume after discharging 40 ampere-hours will be 540 cc. The ampere-hour equivalent of the electrolyte at the end of this discharge will be

$$0.540 \times 62 = 33.5.$$

The ampere-hours initially present were

$$33.5 + 40 = 73.5.$$

The ampere-hour equivalent per liter initially present was, therefore,

$$\frac{73.5}{0.580} = 127.$$

The table shows that this acid was specific gravity 1.274. *Answer.*

6. The electrolyte of a cell of a stationary battery of 280 ampere-hours' capacity has a specific gravity of 1.200 at 25° C. at the conclusion of the charging period. The normal value of the specific gravity in this cell is 1.210. The amount of electrolyte is 40 pounds. How much lead sulphate remains on the plates?

40 pounds of electrolyte = 18.1 kilograms which divided by the specific gravity when fully charged 1.210 = 15.0 liters as the volume initially present. The ampere-hour equivalent for the 1.210 acid is

$$15.0 \times 95 = 1425.$$

As a first approximation, it is necessary to assume the volume of electrolyte at 1.200 sp. gr. to be the same. The ampere-hour equivalent of this is

$$15.0 \times 90 = 1350.$$

The difference is therefore 75 ampere-hours and the volume of electrolyte at 1.200 is corrected to

$$15.0-0.075=14.9.$$

for which the equivalent is

$$14.9\times \quad 90=1341.$$

Since 1 ampere-hour decomposes 3.66 grams of acid, the deficit of acid is

$$(1425-1341)\times 3.66=308 \text{ g.}$$

$$\frac{H_2SO_4}{PbSO_4}=\frac{98}{303}=\frac{308}{951}.$$

Whence there are 951 grams of lead sulphate on the plates. *Answer.*

7. An aviation battery is rated to give 28 ampere-hours at the 5-hour rate. By actual test it was found to give only 24 ampere-hours. The battery contained 210 cc. of electrolyte of specific gravity 1.280 at 25° C. Is this a sufficient amount?

$0.210\times 130=27.3$ ampere-hours, that is, the battery could not give its rated capacity even if the electrolyte could be reduced to water.

g. Viscosity.

A knowledge of the viscosity of sulphuric-acid solutions is important, because the rate of diffusion of the acid through the pores of the plate is dependent upon it. In this respect the viscosity exerts a powerful influence upon the capacity, but it is seldom referred to in this connection. In the following table, the absolute viscosities expressed in poises are given. They have been computed for convenient specific gravities of the electrolyte, from measurements of Rhodes and Barbour.[4] The

TABLE XVI

Viscosity of Solutions of Sulphuric Acid

Specific Gravity	Viscosity Expressed in Poises		
	0° C. (32° F.)	25° C. (77° F.)	50° C. (122° F.)
1.000	0.0180	0.0094	0.0056
1.050	0.0202	0.0107	0.0068
1.100	0.0226	0.0125	0.0077
1.150	0.0260	0.0150	0.0095
1.200	0.0309	0.0180	0.0114
1.250	0.0365	0.0213	0.0143
1.300	0.0423	0.0246	0.0168
1.350	0.0481	0.0276	0.0190
1.400	0.0540	0.0308	0.0209

[4] Jour. Indus. and Engin. Chem., 15, p. 850, 1923.

table shows that the viscosity of the solutions is almost doubled for a drop in temperature of 25° C. (45° F.), and it is at once apparent why the capacity of storage cells falls off so rapidly at low temperatures. The relation of the viscosity to the rate of diffusion is discussed in Chapter V.

3. THE MEASUREMENT OF SULPHURIC-ACID SOLUTIONS

The careful operation of storage batteries requires that the electrolyte should contain the proper amount of sulphuric acid and water. Convenient and accurate means are necessary for measuring the concentration of these solutions. The method most generally used is to measure the specific gravity, or the density of the solution, at some definite temperature. Other methods include the use of arbitrary scales, such as the Baumé or the Twaddell scales. The concentration may also be expressed as the percentage, by weight or volume, of the sulphuric acid in the solution. This is convenient in preparing solutions of a definite strength. Chemical computations are often facilitated when based on the number of gram-equivalents per liter. For storage or shipping purposes, the concentration as it affects the weight and bulk of the packages is important. This requires the pounds per cubic foot or the kilograms per liter.

Table XVIII gives the comparative values of these different methods of measurement.

a. Meaning of Specific Gravity and Density.

The specific gravity of a solution is the ratio of the weight of the solution to the weight of an equal volume of pure water at some fixed temperature. Density, on the other hand, is the ratio of the mass of the liquid to its own volume at a definite temperature. Density measures a property of the substance itself, but specific gravity depends on properties of two substances. Since specific gravity is based on a comparison with water, for which the density at 4° C. is unity, the values for the specific gravity of a solution and its density are very nearly the same.

The specific gravity of sulphuric acid solutions used for the electrolyte varies appreciably with the temperature. It is, therefore, customary to state the specific gravity thus: specific gravity $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$ or specific gravity $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$. The temperature above the line is the temperature of the solution, and the temperature below the line the temperature of the water taken as the standard. A specific gravity

referred to water at its maximum density (4° C.) is identical with the density of the solution. For a solution at 25° C. this would be written specific gravity $\frac{25° \text{ C.}}{4° \text{ C.}}$, or density $\frac{25° \text{ C.}}{4° \text{ C.}}$.

The difference between the specific gravities and the densities, as measured on the various scales in common use, is at most about four units in the third decimal place. For commercial work in storage batteries, this small difference can generally be neglected. Many of the small and cheap hydrometers used for testing automobile batteries do not indicate the basis of their scale. But research and laboratory work, and the operation of large central station batteries require a more exact knowledge. In Table XVII conversion factors to the fourth

TABLE XVII

CONVERSION OF SPECIFIC GRAVITIES AND DENSITIES *

(The table contains factors which are to be used to multiply the observed reading of specific gravity or density to obtain the difference between two scales of measurement. This difference is to be added to or subtracted from the observed reading, according to the plus and minus signs, to obtain the reading converted to the desired basis of measure.)

Converted from	Converted to						
	Density $\frac{25° \text{ C.}}{4° \text{ C.}}$	Density $\frac{20° \text{ C.}}{4° \text{ C.}}$	Density $\frac{15° \text{ C.}}{4° \text{ C.}}$	Sp. Gr. $\frac{15° \text{ C.}}{15° \text{ C.}}$	Sp. Gr. $\frac{60° \text{ F.}}{60 \text{ °F.}}$	Sp. Gr. $\frac{20° \text{ C.}}{20° \text{ C.}}$	Sp. Gr. $\frac{25° \text{ C.}}{25° \text{ C.}}$
Density $\frac{25° \text{ C.}}{4° \text{ C.}}$	0	+0.0001	+0.0002	+0.0011	+0.0012	+0.0019	+0.0029
Density $\frac{20° \text{ C.}}{4° \text{ C.}}$	−0.0001	0	+0.0001	+0.0010	+0.0011	+0.0018	+0.0028
Density $\frac{15° \text{ C.}}{4° \text{ C.}}$	−0.0002	−0.0001	0	+0.0009	+0.0010	+0.0017	+0.0027
Sp. Gr. $\frac{15° \text{ C.}}{15° \text{ C.}}$	−0.0011	−0.0010	−0.0009	0	+0.0001	+0.0008	+0.0018
Sp. Gr. $\frac{60° \text{ F.}}{60° \text{ F.}}$	−0.0012	−0.0011	−0.0010	−0.0001	0	+0.0007	+0.0017
Sp. Gr. $\frac{20° \text{ C.}}{20° \text{ C.}}$	−0.0019	−0.0018	−0.0017	−0.0008	−0.0007	0	+0.0010
Sp. Gr. $\frac{25° \text{ C.}}{25° \text{ C.}}$	−0.0029	−0.0028	−0.0027	−0.0018	−0.0017	−0.0010	0

* Based on data contained in Circular 19 of the Bureau of Standards.

decimal place are given for the scales in most frequent use. The method of using this table may be seen from the following example: A hydrometer reading density $\frac{20^\circ\text{ C.}}{4^\circ\text{ C.}}$ is used to measure a solution of which the specific gravity $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$ is desired. If the density reading is 1.280, what is the specific gravity?

$$\text{Specific gravity } \frac{25^\circ\text{ C.}}{25^\circ\text{ C.}} = \text{density } \frac{20^\circ\text{ C.}}{4^\circ\text{ C.}} + \left(\text{factor} \times \text{density } \frac{20^\circ\text{ C.}}{4^\circ\text{ C.}}\right)$$
$$= 1.280 + (0.0028 \times 1.280) = 1.284$$

Specific gravities of storage-battery electrolytes are usually expressed to the third decimal place, one unit in the last place being called a "point." Thus solutions of 1.285 and 1.270 sp. gr. are said to differ by 15 points. Colloquial expressions, such as "twelve-eighty acid" or "thirteen hundred acid," refer to solutions of 1.280 and 1.300 sp. gr.

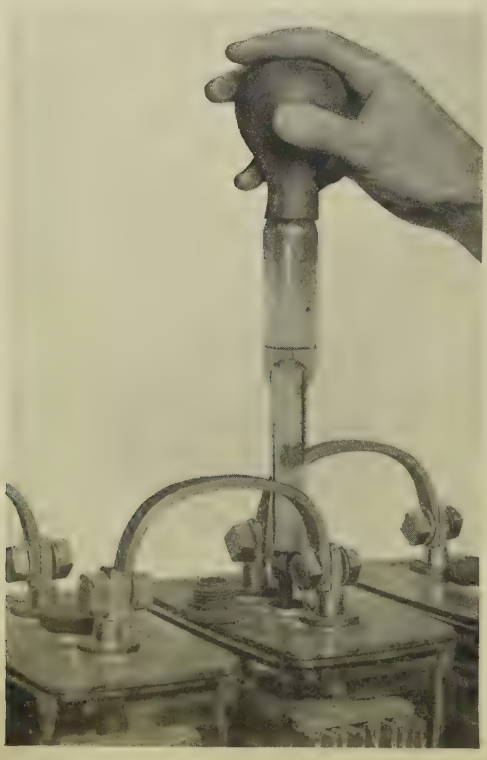

Fig. 39.—Use of the syringe hydrometer.

The specific gravity of the electrolyte decreases with increasing temperature. The temperature coefficient is not a constant quantity, but varies with the specific gravity. In Table XVIII the values of this coefficient per degree Centigrade and per degree Fahrenheit are given for each value of the specific gravity. The coefficient applies strictly to specific gravities referred to water at 15° C., but for practical purposes may be used for the 25° basis also. This coefficient does not, however, convert specific gravities at $\frac{15^\circ}{15^\circ}$ to the $\frac{25^\circ}{25^\circ}$ basis. The familiar rule that there is a change of one

point for each 3° F. difference from the standard temperature is correct only for solutions of 1.150 sp. gr. For greater concentrations the correction is larger. At 1.280 sp. gr. it is two points for 5° F., or three points for 4° C. When the temperature of the solution is above the standard temperature, the correction is to be added, and when below, subtracted from the observed specific gravity to reduce this to the correct reading at the standard temperature.

Specific gravities for storage-battery purposes are most conveniently measured by means of hydrometers. These are of several varieties, but all consist of a float of some kind. For stationary batteries, the hydrometer is immersed in the liquid of the cell itself, and in some cases has a recording attachment. Hydrometers for use with portable batteries are usually of the syringe type (Fig. 39), which permits drawing a portion of the electrolyte from the cell into a tube of glass in which the hydrometer is confined. After the reading is completed the solution is replaced in the cell from which it was drawn.

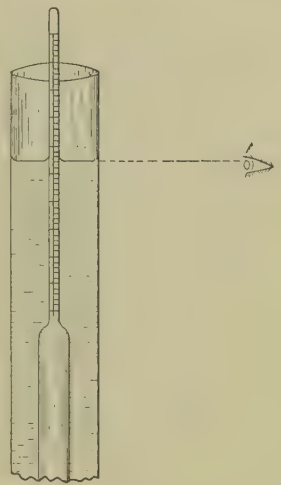

FIG. 40.—Proper position of the eye for reading a hydrometer.

A well-designed hydrometer should be made of smooth, transparent glass, circular in cross-section along the axis, with fixed ballast, and a scale on ledger paper with graduation that is correct to within one-half of the smallest division.[5] Flat hydrometers that will float between the plates and jar of stationary cells are also used. The hydrometer should float vertically and indicate the basis of its scale as, for example, specific gravity $\frac{15° \text{ C.}}{15° \text{ C.}}$ In making readings of a hydrometer the eye should be level with the surface of the liquid, disregarding the curvature due to the surface tension, as shown in Fig. 40.

b. The Baumé and Twaddell Scales.

The standard Baumé scale, for liquids heavier than water, as used in the United States, is related to the specific gravity by the following equation:

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Specific gravity } \frac{60° \text{ F.}}{60° \text{ F.}}}$$

[5] Circular No. 16, p. 5, Bureau of Standards.

TABLE XVIII

MEASUREMENT OF SULPHURIC ACID SOLUTIONS

Specific Gravity, 15° C. / 15° C.	Specific Gravity, 25° C. / 25° C.	Temperature Coefficient of Sp. Gr. 15° C. Per ° C.	Temperature Coefficient of Sp. Gr. 15° C. Per ° F.	Per Cent H_2SO_4 by Weight	Per Cent H_2SO_4 by Volume	Baumé Degrees	Twaddell Degrees	Pounds per Cubic Foot	Kilograms per Liter
1.000	1.000	.....	.....	0.0	0.0	0.0	0	62.4	
1.010	1.009	(.00018)	(.00010)	1.4	0.8	1.4	2	63.0	
1.020	1.019	(22)	(12)	2.9	1.6	2.8	4	63.6	
1.030	1.029	(26)	(14)	4.4	2.5	4.2	6	64.2	
1.040	1.039	(29)	(16)	5.9	3.3	5.6	8	64.8	
1.050	1.049	(33)	(18)	7.3	4.2	6.9	10	65.5	
1.060	1.058	36	20	8.7	5.0	8.2	12	66.1	
1.070	1.068	40	22	10.1	5.9	9.5	14	66.7	
1.080	1.078	43	24	11.5	6.7	10.7	16	67.4	
1.090	1.088	46	26	12.9	7.6	12.0	18	68.0	
1.100	1.097	48	27	14.3	8.5	13.2	20	68.6	
1.110	1.107	51	28	15.7	9.5	14.4	22	69.2	
1.120	1.117	53	29	17.0	10.3	15.5	24	69.8	
1.130	1.127	55	31	18.3	11.2	16.7	26	70.5	
1.140	1.137	58	32	19.6	12.1	17.8	28	71.1	
1.150	1.146	60	33	20.9	13.0	18.9	30	71.7	
1.160	1.156	62	34	22.1	13.9	20.0	32	72.4	
1.170	1.166	63	35	23.4	14.9	21.1	34	73.0	
1.180	1.176	65	36	24.7	15.8	22.1	36	73.6	
1.190	1.186	66	37	25.9	16.7	23.2	38	74.2	
1.200	1.196	68	38	27.2	17.7	24.2	40	74.8	
1.210	1.206	69	38	28.4	18.7	25.2	42	75.4	
1.220	1.216	70	39	29.6	19.6	26.1	44	76.1	
1.230	1.225	71	39	30.8	20.6	27.1	46	76.7	
1.240	1.235	72	40	32.0	21.6	28.1	48	77.3	
1.250	1.245	72	40	33.2	22.6	29.0	50	78.0	
1.260	1.255	73	40	34.4	23.6	29.9	52	78.6	
1.270	1.265	73	41	35.6	24.6	30.8	54	79.2	
1.280	1.275	74	41	36.8	25.6	31.7	56	79.8	
1.290	1.285	74	41	38.0	26.6	32.6	58	80.4	

Approximately equal numerically to the specific gravity; for example, a solution of 1.300 sp. gr. will weigh approximately 1.300 kg. per liter.

TABLE XVIII—*Continued*

MEASUREMENT OF SULPHURIC-ACID SOLUTIONS

Specific Gravity, 15° C. / 15° C.	Specific Gravity, 25° C. / 25° C.	Temperature Coefficient of Sp. Gr. 15° C.		Per Cent H_2SO_4 by Weight	Per Cent H_2SO_4 by Volume	Baumé Degrees	Twaddell Degrees	Pounds per Cubic Foot	Kilograms per Liter
		Per ° C.	Per ° F.						
1.300	1.295	.00075	.00042	39.1	27.6	33.5	60	81.0	
1.310	1.305	75	42	40.3	28.7	34.3	62	81.7	
1.320	1.315	76	42	41.4	29.7	35.2	64	82.3	
1.330	1.325	76	42	42.5	30.7	36.0	66	82.9	
1.340	1.335	76	42	43.6	31.8	36.8	68	83.6	
1.350	1.345	77	43	44.7	32.8	37.6	70	84.2	
1.360	1.355	77	43	45.8	33.9	38.4	72	84.8	
1.370	1.365	78	43	46.9	34.9	39.2	74	85.4	
1.380	1.375	78	43	47.9	35.9	39.9	76	86.1	
1.390	1.385	79	44	49.0	37.0	40.7	78	86.7	
1.400	1.395	79	44	50.0	38.0	41.4	80	87.3	
1.410	1.405	80	44	51.0	39.1	42.2	82	88.0	
1.420	1.415	80	45	52.0	40.1	42.9	84	88.6	
1.430	1.425	81	45	53.0	41.2	43.6	86	89.2	
1.440	1.435	81	45	54.0	42.2	44.3	88	89.8	
1.450	1.445	82	46	54.9	43.3	45.0	90	90.4	
1.460	1.455	83	46	55.9	44.4	45.7	92	91.0	
1.470	1.465	83	46	56.9	45.5	46.4	94	91.7	
1.480	1.475	84	47	57.8	46.5	47.0	96	92.3	
1.490	1.485	85	47	58.7	47.5	47.7	98	93.0	
1.500	1.495	85	47	59.7	48.7	48.3	100	93.6	
1.510	1.505	86	48	60.6	49.7	49.0	102	94.2	
1.520	1.515	87	48	61.5	50.8	49.6	104	94.8	
1.530	1.525	87	48	62.4	51.9	50.2	106	95.4	
1.540	1.535	88	49	63.3	53.0	50.8	108	96.0	
1.550	1.545	89	49	64.2	54.1	51.5	110	96.7	
1.560	1.554	89	49	65.1	55.2	52.1	112	97.3	
1.570	1.564	90	50	66.0	56.3	52.6	114	98.0	
1.580	1.574	91	50	66.8	57.4	53.2	116	98.6	
1.590	1.584	91	51	67.7	58.5	53.8	118	99.2	

Approximately equal numerically to the specific gravity; for example, a solution of 1.300 sp. gr. will weigh approximately 1.300 kg. per liter

TABLE XVIII—*Continued*

MEASUREMENT OF SULPHURIC-ACID SOLUTIONS

Specific Gravity, $\frac{15° C.}{15° C.}$	Specific Gravity, $\frac{25° C.}{25° C.}$	Temperature Coefficient of Sp. Gr. 15° C.		Per Cent H_2SO_4 by Weight	Per Cent H_2SO_4 by Volume	Baumé Degrees	Twaddell Degrees	Pounds per Cubic Foot	Kilograms per Liter
		Per ° C.	Per ° F.						
1.600	1.594	.00092	.00051	68.6	59.7	54.4	120	99.8	
1.610	1.604	93	51	69.4	60.8	54.9	122	100.4	
1.620	1.614	93	52	70.3	61.9	55.5	124	101.0	
1.630	1.624	94	52	71.2	63.1	56.0	126	101.7	
1.640	1.634	95	53	72.0	64.2	56.6	128	102.3	
1.650	1.644	95	53	72.9	65.4	57.1	130	102.9	
1.660	1.654	96	53	73.7	66.5	57.7	132	103.6	
1.670	1.664	97	54	74.5	67.6	58.2	134	104.2	
1.680	1.674	98	54	75.4	68.8	58.7	136	104.8	
1.690	1.684	.00099	55	76.2	70.0	59.2	138	105.4	
1.700	1.694	.00100	55	77.1	71.2	59.7	140	106.0	
1.710	1.704	101	56	77.9	72.4	60.2	142	106.7	
1.720	1.713	102	57	78.8	73.6	60.7	144	107.3	
1.730	1.723	103	58	79.7	75.0	61.2	146	108.0	
1.740	1.733	105	59	80.6	76.2	61.7	148	108.6	
1.750	1.743	107	60	81.5	77.6	62.1	150	109.2	
1.760	1.753	109	60	82.4	78.8	62.6	152	109.8	
1.770	1.763	110	61	83.4	80.2	63.1	154	110.4	
1.780	1.773	110	61	84.4	81.7	63.5	156	111.0	
1.790	1.783	111	62	85.6	83.3	64.0	158	111.7	
1.800	1.793	110	61	86.7	84.8	64.4	160	112.3	
1.810	1.803	109	61	88.1	86.7	64.9	162	112.9	
1.820	1.813	108	60	89.8	88.9	65.3	164	113.5	
1.830	1.823	106	59	91.8	91.4	65.8	166	114.1	
1.840	1.834	.00103	.00057	94.8	94.8	....	168	114.8	

Approximately equal numerically to the specific gravity; for example, a solution of 1.300 sp. gr. will weigh approximately 1.300 kg. per liter

EXPLANATION OF THE TABLE

COLUMN 1.—Specific gravities of solutions are given at $\frac{15° C.}{15° C.}$, which is approximately equal to $\frac{60° F.}{60° F.}$ Hydrometers which are used for measuring sulphuric-acid solutions are frequently standardized at 60° F.

COLUMN 2.—Specific gravities of solutions corresponding to those given in Column 1 are given at $\frac{25^\circ\text{ C.}}{25^\circ\text{ C.}}$ $\left(\frac{77^\circ\text{ F.}}{77^\circ\text{ F.}}\right)$.

COLUMNS 3 AND 4.—Contain the temperature coefficients to calculate the specific gravity for any temperature $t°$ from the specific gravities given for 15° C. Values are given for both Centigrade and Fahrenheit degrees. They have been calculated from Domke's Tables, Wiss. Abh. Normal Eichungs Kom., 5, p. 75 (1904). Let the required specific gravity at $t°$ be represented by S_t; the specific gravity of the solution at 15° by S_{15} and the temperature coefficient by α, then

$$S_t = S_{15} + \alpha(15^\circ - t^\circ).$$

The temperature cofficient for temperatures other than 15°, which may be taken as standard, varies slightly with the temperature. For solutions of the specific gravities most commonly used in storage batteries, the values given in the table may be assumed to be correct to within 3 per cent for a range of temperature from 0° C. to 45° C. Values in parenthesis were obtained by extrapolation.

COLUMN 5.—Per cent by *weight* of H_2SO_4 solutions corresponding to those given in Column 1. These were computed from Domke's Tables, pp. 131–148.

COLUMN 6.—Per cent by *volume* of H_2SO_4 solutions corresponding to those given in Column 1. These were computed from the formula:

$$\text{Per cent by volume} = \frac{d}{1.840} \times \text{per cent by weight.}$$

Values of d, the specific gravity of solutions for given percentages of H_2SO_4 by weight, were based on Domke's tables and the computations checked by comparison with Pickering's contraction table. J. Chem. Soc., Vol. 57, p. 148, 1890.

COLUMN 7.—Baumé degrees corresponding to the specific gravities given in Column 1 calculated from the formula:

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{Specific gravity } \frac{60^\circ\text{ F.}}{60^\circ\text{ F.}}}.$$

COLUMN 8.—Twaddell degrees calculated from the formula:

$$\text{Degrees Twaddell} = 200\left(\text{specific gravity } \frac{60^\circ\text{ F.}}{60^\circ\text{ F.}} - 1\right).$$

COLUMN 9.—Pounds per cubic foot of solutions having the specific gravities given in Column 1.

COLUMN 10.—The kilograms per liter are equal numerically to the specific gravity, if it be assumed that the difference between the specific gravity $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$ and the density $\frac{15^\circ\text{ C.}}{4^\circ\text{ C.}}$ is negligible. For example, the

Specific gravity $\frac{15^\circ\text{ C.}}{15^\circ\text{ C.}}$ for 38 per cent acid is 1.29027,

Density $\frac{15^\circ\text{ C.}}{4^\circ\text{ C.}}$ for 38 per cent acid is 1.28915

Difference 0.00112

The assumption is correct, therefore, to a unit in the third decimal place.

The number 145 is called the modulus. Great confusion [6] has resulted from the variety of values assigned to it.

[6] Circular No. 59, Bureau of Standards.

The Baumé scale is now obsolete in this country for storage-battery work, but it is frequently referred to in foreign books on the subject. The Twaddell scale, extensively used in England, is related to the specific gravity in a more definite way. One degree Twaddell is equal to five units in the third decimal place of the specific gravity, from which it is apparent that the relation may be expressed by the equation:

$$\text{Degrees Twaddell} = \frac{\text{Specific gravity} - 1}{5} \times 1000$$

The use of specific gravities is preferable, in storage-battery work, to any of the arbitrary scales.

4. PREPARATION OF THE ELECTROLYTE

The electrolyte for lead batteries is prepared by diluting pure sulphuric acid with pure water. The acid is ordinarily sold as the concentrated acid of specific gravity 1.835 to 1.840 or partially diluted to 1.400. The latter is more bulky, which is a disadvantage in shipment, but it possesses a marked advantage in being easier to prepare for use. (See p. 77.) When the concentrated acid is diluted, the solution becomes very hot. The acid should always be poured into the water, never the water into the acid, because of the danger to the person making the mixture. Although the amount of heat evolved in either case is the same, the specific heats of water and of concentrated acid are quite different, as was shown in Table X. A stream of water flowing into the concentrated acid causes the liberation of a great amount of heat, which, because of the low specific heat of the acid, causes a large local rise in temperature. Acid flowing into water cannot cause so great a rise in temperature, because the specific heat of the water is high. The solution should be stirred continually while the acid is being poured into the water, to prevent the heavier acid from flowing to the bottom of the vessel without mixing with the water. Suitable vessels for use in mixing or storing small quantities of the electrolyte are of china, vitreous earthenware, or glass. These are subject to cracking, and lead-lined tanks are preferred, especially for larger quantities. No metallic vessel other than lead should be used.

After diluting the acid, it is necessary to wait until the mixture has cooled before pouring it into the battery, to avoid injury to the plates and separators. The cooling may be hastened by a jet of compressed air, but the air must be pure. The great rise in temperature which occurs when the acid and water are mixed may be avoided altogether by using ice made from distilled water, instead of water. This is because the

latent heat of fusion of the ice is approximately equal to the heat liberated by the dilution of the sulphuric acid. The ice, if drained of surplus water, may be added directly to the acid. In an experiment, 220 grams of ice were added to 98 grams of concentrated acid at room temperature. The temperature of the mixture was found to be $-2°$ C. after all the ice had melted. The specific gravity of this mixture at 25° C. was 1.225. Since the latent heat of fusion of the ice is 79.63 gram-calories, the total heat absorbed by the ice was $220 \times 79.63 = 17{,}518$ gram-calories. The total heat liberated by the dilution of the acid was, by interpolation of the values given in Table X, 15,600 gram-calories. The excess of heat absorbed indicates that the solution would be below 0° C., as was observed.

To facilitate the preparation of electrolytes of any required concentration, Fig. 41 shows the relative proportions of acid and water neces-

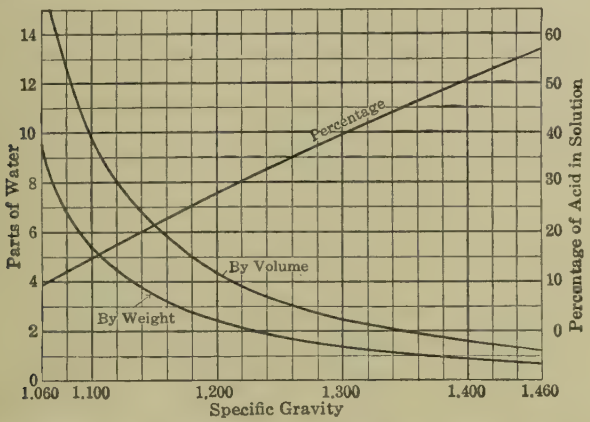

FIG. 41.—Preparation of electrolyte of any specific gravity from concentrated acid of 1.835 sp. gr.

sary. Manufacturers ordinarily furnish information as to the proper strength to be used in any particular battery.

It is often necessary to change the specific gravity of a solution of sulphuric acid by a given amount. The amount of water or acid which must be added to make the desired change can be calculated easily by using Table XVIII. For example: 290 pounds of electrolyte at 25° C. are to be raised from 1.255 sp. gr. to 1.295 sp. gr. How much acid must be added?

By the table, 1.295 would contain 39.2 per cent acid or 60.8 per cent water

and 1.255 contains 34.4 per cent acid or 65.6 per cent water

The excess of water is, by subtraction, 4.8 per cent; or

$$290 \times 4.8 \text{ per cent} = 13.92 \text{ pounds.}$$

The amount of acid to be added is

$$\frac{100 \times 13.92}{60.8} = 22.9 \text{ pounds.}$$

As another example, 340 pounds of electrolyte at 25° C. of 1.325 sp. gr. are to be reduced to 1.285 sp. gr. How much water is to be added?

By the table, 1.325 contains 42.6 per cent acid

and 1.285 would contain 38.0 per cent acid

The excess of acid is, by subtraction, 4.6 per cent; or

$$340 \times 4.6 \text{ per cent} = 15.65 \text{ pounds.}$$

The amount of water to be added is

$$\frac{100 \times 15.65}{38.0} = 41.1 \text{ pounds.}$$

5. THE CHOICE OF SPECIFIC GRAVITIES FOR BATTERY SERVICE

It is a matter of common observation that the specific gravity of the electrolyte in portable batteries is higher than in stationary batteries, but the choice does not depend entirely on space and weight considerations. Chemical reactions, temperature, and the character of service are of importance in determining the proper specific gravity.

The first requirement is that the concentration be sufficient to provide enough acid in a given space within the cell to give the required output. The theoretical number of ampere-hours per liter has been calculated for various concentrations and given in Table XV. It is not possible, however, to use all the acid in the cell, because the resistance of the cell would increase to a high value and the voltage would fall rapidly if the electrolyte became too impoverished. Space and weight requirements for portable cells do not permit of large quantities of electrolyte. It is evident that high specific gravities are desirable for these, in contrast to the stationary cells for which space and weight are of less importance.

Chemical reactions, occurring within the cell during the time that it is at rest, place a limitation on the concentrations of acid that may be used. Local action (p. 102) increases rapidly when the concentration of the acid is increased. This is particularly true of the negative plate, where a reaction takes place between the sponge lead and the sulphuric

acid. Another chemical action taking place within the cell is the action of the electrolyte on the separators, which are usually made of wood. These separators are destroyed by too strong acid. The action of 1.300 sp. gr. acid on the separator is much more marked than that of 1.250 and lower concentrations. The effect of certain impurities which increase local action is obviously decreased by reducing the concentration. The chemical reactions within the cell practically limit the higher concentrations to 1.300 sp. gr.

The temperatures to which the battery is subjected in service have an important bearing on the specific gravity. Batteries exposed to low temperatures, such as automobile batteries in cold climates or aeroplane batteries, require a high density of acid to permit their capacity to be utilized without depleting their electrolyte to so low a specific gravity that freezing occurs. An inspection of Fig. 13 shows that little is to be gained by increasing the specific gravity above 1.300 at 25° C. If the specific gravity were made 1.350 at 25° C., a decrease of 120 points during discharge might take place without raising the freezing point above −40° C. (−40° F.), but such a battery would deteriorate rapidly if brought to room temperature. On the other hand, batteries for use in hot climates or on ships passing through the tropics, require a lower specific gravity because of the increased chemical activity at the higher temperatures.

The character of the service has an important bearing also on the best value for the specific gravity. The performance of batteries that are charged and discharged at frequent intervals, such as starting and lighting batteries or vehicle batteries, is not seriously affected by slight chemical actions resulting in the formation of lead sulphate. Stationary batteries, however, which are less frequently charged, must be free from local action so far as possible. Batteries intended for high discharge rates should be provided with acid of greater concentration than those for " normal " discharge rates, because the capacity at the high rates of discharge increases with the concentration (p. 199).

The range of concentrations for different types of batteries when fully charged is approximately as follows:

Stationary batteries	1.200 to 1.225
Truck and tractor batteries	1.270 to 1.300
Starting and lighting batteries	1.270 to 1.300
Ditto in the tropics	1.200 to 1.230
Aviation batteries	1.280 to 1.300
Car lighting batteries	1.210 to 1.230
Portable railway signal batteries	1.220
Countercells	1.210 to 1.250

6. PURITY OF THE ELECTROLYTE

The most satisfactory service can only be obtained when the electrolyte is of a high degree of purity. It is necessary, therefore, that both the sulphuric acid and the water which are used in preparing the electrolyte should be pure. Distilled water is much to be preferred to natural water. The impurities which are contained in natural water may be small in amount, but their effect in the storage battery is cumulative because the evaporation which takes place results only in the loss of oxygen and hydrogen which are the constituents of water, leaving the mineral and other impurities in the solution. Natural waters vary considerably in composition from one time of the year to another. The ordinary impurities which natural waters contain are nitrates and other compounds of nitrogen, chlorides, sulphates, bicarbonates, oxides of iron, aluminum, silicon, sodium, potassium, magnesium, and calcium. It has been found possible to use natural water for storage-battery purposes in certain localities, but it is not advisable to make this a general rule because of the varying composition of the water in different localities. Distilled water is always to be recommended when it is possible to obtain it. Rain water may be used in some cases if not collected from metallic roofs. Impurities found in the electrolyte often are derived from the plates, if the materials used in their manufacture are not pure.

(a) Local Action.

The discharge of either the positive or negative plates in sulphuric-acid solutions results primarily in the formation of lead sulphate. A certain amount of lead sulphate is formed as the result of local action whenever the plates are immersed in any acid solution, even though it be the purest obtainable. Detrimental impurities may (1) corrode the plate, (2) accelerate the formation of lead sulphate, or (3) be deposited in the pores of the plate. In any case the weight of the plate changes and this change affords the most sensitive and exact means we have for estimating the extent of the reaction. This method was devised by Vinal and Ritchie [7] for measurements on positive and negative plates suspended in pure sulphuric-acid solutions.

In order to obtain comparable results, it is necessary that the temperature be maintained at a constant value. This was accomplished by immersing the glass jars containing the electrolytes in a large water bath thermostatically controlled at 25° C. (77° F.). This temperature was

[7] Bureau of Standards Technologic Paper No. 225; Chem. and Met. 27, p. 1116; Electrical World, 80, p. 1383, 1922.

maintained constant to within about 0.01° C. Two positive plates or two negative plates, suspended on glass hooks, were placed in each jar. As a preliminary step the plates were given several cycles of charge and discharge, following which they were fully charged and then submerged in the electrolytes to be tested. Each jar contained a solution of chemically pure sulphuric acid. The electrolytes were saturated

FIG. 42.—Apparatus for determining the rate of sulphation of storage-battery plates.

with lead sulphate because the previous work showed this to be necessary.

A sensitive balance mounted on a marble slab above the thermostat bath was used for weighing the plates while they were immersed. Any plate could be brought directly under the arm of the balance, as the jars containing them were carried on a revolving frame. The arrangement of the apparatus is shown in Fig. 42.

Since the weighings were made in the electrolyte, a buoyancy correc-

tion was necessary. This correction has been calculated on the basis that the materials have the following densities:

Lead		11.3
Lead sulphate		6.3
Lead peroxide	A plates	8.7
	B plates	8.8

The buoyancy corrections are applied to a small difference of two weighings, and hence a slight error in the density of either the solutions or the active materials produces a negligible error in the final result.

Since the molecular weight of lead is 207.20 and that of lead sulphate 303.26, the gain in weight during the transformation of 1 mol of lead to lead sulphate is 96.06 grams; and the relative gain in weight is $\frac{96.06}{207.20}$ times the weight of lead acted upon. There is, of course, a large amount of lead which does not take part in the reaction and which decreases the sensibility of the weighings; but in spite of this fact and the heavy damping resulting from the viscosity of the electrolytes, the balance was sufficiently sensitive to permit an accuracy of a few tenths of a milligram to be obtained.

From the rate of change in weight of the plates, the equivalent loss in ampere-hour capacity can be computed. The valence is 2, and hence a gain in weight of the negative plate of 96.06 grams is equivalent to $2\times96{,}500$ coulombs. From this the change in weight is computed to be 1.79 grams per ampere-hour.

The effect of temperature and concentration on the rate of sulphation is important. In Table XIX are given the measurements made on the negative plates of two manufacturers when the solutions were maintained at constant temperatures of 22°, 25°, and 30° C. The increase in the rate of sulphation from 22° to 25° C. is proportionately greater than from 25° to 30° C.

Both chemical and electrochemical reactions are possible at the negative plate, but the former are probably predominant over the latter during self-discharge. This is indicated by the results for the A plates in 1.150 and 1.400 acid. The gain in weight per hour in the stronger acid is 23 times that in the more dilute. The change in potential of a lead plate as the concentration of the electrolyte is changed from 1.150 to 1.400 sp. gr. acid is less than 0.1 volt, according to the measurements of Gladstone and Hibbert.[8] The resistivity of the more concentrated electrolyte is higher than for the 1.150 sp. gr. electrolyte. On the basis of Ohm's law, therefore, this marked increase in the extent

[8] Jour. Inst. Elec. Eng., 21, p. 430, 1892.

of the reaction cannot be readily accounted for as an electrochemical reaction.

TABLE XIX

EFFECT OF TEMPERATURE ON THE RATE OF SULPHATION OF NEGATIVE PLATES

Specific Gravity $\frac{25°}{25°}$	Gain in Weight, Grams per Hour, Saturated Solutions, for Plates of					
	Manufacturer B at			Manufacturer A at		
	22° C.	25° C.	30° C.	22° C.	25° C.	30° C.
1.150	0.0031	0.0048	0.0056	0.0012	0.0022	0.0022
1.200	0.0073	0.0118	0.0118	0.0016	0.0026	0.0027
1.250	0.0111	0.0178	0.0196	0.0028	0.0036	0.0051
1.300	0.0183	0.0283	0.0325	0.0046	0.0060	0.0082
1.350	0.0270	0.0385	0.0420	0.0122	0.0151	0.0196
1.400	0.0614	0.0906	0.1027	0.0350	0.0460	0.0544

The initial rate of sulphation, particularly in the solutions that were unsaturated with lead sulphate, was somewhat greater than is shown in Table XIX. It can easily be computed that the capacity of the plates would be exhausted in a relatively short time if the initial rate of sulphation were to continue indefinitely. The decrease in the rate of sulphation is probably to be attributed to the protection which the lead sulphate affords to the underlying active material and also to the increasing amount of lead sulphate present in the solutions which were initially unsaturated.

Local action at the positive plate is essentially electrochemical, resulting from the difference in potential between the oxide and the lead-antimony alloy of the grid. Metallic impurities are not precipitated by the oxide, and Dolezalek and Finckh [9] have stated that no solubility of the peroxide in solutions of the specific gravities ordinarily used in storage batteries can be detected. The reaction at the positive plate in these experiments is therefore to be regarded as the general expression for the discharge of a cell, with the qualification that the negative electrode may be lead or lead-antimony alloy, depending on the construction of the plate.

$$PbO_2 + Pb + 2H_2SO_4 = 2PbSO_4 + 2H_2O$$

The lead sulphate formed appears on both the peroxide and the grid.

[9] Zeit. f. Anorg. Chem., 51, p. 320, 1906.

The gain in weight of the positive plates is not as simply related to the total amount of sulphate formed as in the case of the negatives. The sulphate which forms on the grid or the underlying lead is equal to 96.06 grams for $2\times96{,}500$ coulombs, but the change in weight of the positive plates because of the formation of sulphate on the peroxide is 64.06 grams for the same quantity of electricity. The difference is accounted for by the formation of 2 mols of water at the peroxide. This means that 160.12 grams of sulphate would be formed on the positive plate if the quantity of electricity flowing were $2\times96{,}500$ coulombs. The ampere-hour equivalent for the gain in weight resulting from local action is, therefore, 2.99 grams for each ampere-hour. The experimental results for the positive plates in solutions of varying concentration at 25° C. are given in Table XX for solutions saturated with lead sulphate.

TABLE XX

Gain in Weight, Grams per Hour, of positive Plates in Solutions at 25° C. Saturated with Lead Sulphate

Specific Gravity $\frac{25°}{25°}$	Gain in Weight for Plates of	
	Manufacturer A	Manufacturer B
1.150	0.0128	0.0077
1.200	0.0121	0.0077
1.250	0.0069	0.0047
1.300	0.0053	0.0050
1.350	0.0050	0.0048
1.400	0.0047	0.0049

It will be observed from the results given in Table XX that the gain in weight of the positive plates decreases as the concentration of the solution increases. This suggests that the plates contained some soluble constituent, the solubility of which increased as the concentration increased, but the data which are available on the solubility of lead peroxide and lead oxide fail to offer an explanation.

(b) Effect of Various Impurities.

The importance of obtaining exact information about the effect of impurities in storage-battery electrolytes arises from the detrimental effects which many of them produce on the operating characteristics and life of the storage battery, and such information is necessary as a basis

for the preparation of specifications for sulphuric acid to be used in the batteries. Engineers have recognized for a long time the necessity for maintaining a high standard of purity in the electrolyte, but within recent years millions of small batteries have passed into the hands of non-technical users who must depend upon the manufacturers and their subsidiaries for satisfactory service.

A determination of the effect of certain impurities has been made by Vinal and Altrup,[10] whose apparatus and methods were the same as those described above. Their experiments included the effect of copper, platinum, iron, and manganese.

A carefully measured quantity of the impurity was added to the electrolyte in each case before the plates were immersed. Simultaneously with the tests to determine the effect of the impurities, measurements were made of the rate of sulphation of the plates in pure solutions. The results of the experiments are shown by means of curves relating the total change in weight of the plates to the time in hours. Weighings of the plates were taken immediately after they were placed in the solutions, and they were weighed at frequent intervals during the first day because the rate of the reaction was generally the greatest at this time. As the reaction slowed down, weighings were made at less frequent intervals. The concentrations of the impurities are expressed as percentages by weight.

Effect of Copper.—The solutions initially had the characteristic blue color of copper sulphate. When the two negative plates were immersed in the solutions, the copper began to deposit upon the plates and the solutions gradually lost color. An analysis of the solutions after the experiment was completed showed only a small trace of copper. This shows that practically all the copper had been deposited upon the plates. Since the amount of solution in which they were immersed greatly exceeded the amount of solution that would ordinarily be present in a battery, the amount of copper on each plate was in excess of that which would be found in ordinary practice. The quantity of solution was approximately ten times the amount for the same number of plates in a starting and lighting battery. To obtain equivalent conditions, therefore, in the case of those impurities which deposit upon the plates, the concentrations should be multiplied by a factor of 10.

The deposition of the copper upon the negative plates could be easily seen. The local action which occurred at the plate as the result of the deposition of copper was accompanied by the evolution of hydrogen. The changes in weight of the plate during the process are shown in the curves of Fig. 43.

[10] Jour. Amer. Inst. Elec. Eng., 1924.

During the first part of the experiment, the extent of the local action produced by the copper is not as great as might be expected. This is probably due to the rather high over-voltage for hydrogen on the surface of copper.

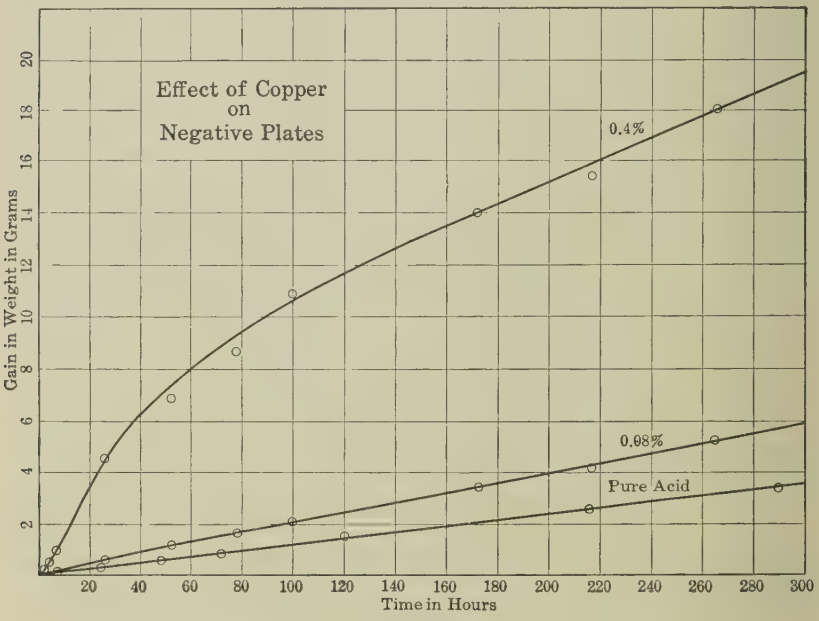

FIG. 43.—Local action of plates in solutions containing copper.

Effect of Platinum.—Platinum has always been considered one of the most deleterious impurities. Platinum, however, is not as common an impurity at the present time as it has been in the past, because comparatively little sulphuric acid is now concentrated in platinum vessels during the process of manufacture.

The platinum evidently began to deposit upon the negative plates very quickly, as they began to gas almost immediately. The plates in solutions containing the greatest amount of platinum gassed violently and increased in weight very rapidly. The gassing was so violent that the surface of the plates was apparently blasted off and most of the platinum thereby eliminated. With the highest concentration the plates became about 60 per cent discharged within eight hours, but after this the rate of their discharge was comparatively slow. The reaction was not quite so violent in the solutions containing the next lower percentage of platinum, but it is significant that the reaction proceeded farther. At the end of forty-eight hours the plates were

72 per cent discharged. The solution containing 0.00003 per cent of platinum produced a reaction which was much slower, but it produced 95 per cent of the ultimate discharge in 1000 hours, calculated on the basis of 60 per cent sulphation of the total amount of active material. The lower concentrations produced smaller effects, but the gain in weight was appreciably greater than with pure acid. One part in ten million, or 0.00001 per cent platinum, produced an increase of 50 per cent in the local action over that in pure acid solutions, which

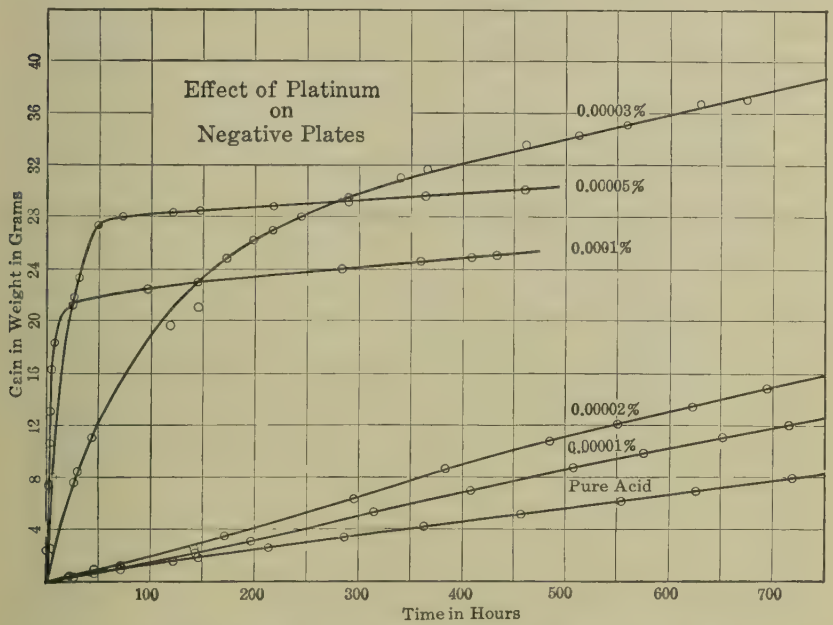

Fig. 44.—Local action of plates in solutions contaminated with small amounts of platinum.

shows that the effect of extremely small amounts of platinum may be detected by this method. Chemically it is possible to determine platinum in solutions to the extent of about one part in two million, but it is estimated that by this method the effect of as little as one part in fifty million may be determined.

The curves of Fig. 44 make possible an estimate of the local action in terms of the equivalent current that would be discharged by the plate normally for the same rate of sulphation. The equivalent currents are proportional to the slopes of the lines. The curve for plates in pure acid shows the average equivalent current of the local action to be 0.0059 ampere. With this as a basis, the equivalent currents during the

first part of the experiment for the other curves have been calculated to be as follows:

Platinum Concentration Per Cent	Current Equivalent of Local Action, Amperes
0.00001	0.0093
0.00002	0.0113
0.00003	0.107
0.00005	0.345
0.00010	1.71

By this calculation, a physical meaning is given to the rather vague term " local action."

Effect of Iron.—Iron may exist in the sulphuric-acid solutions in two states of oxidation. Iron in the ferric condition is reduced to the ferrous condition at the negative plate, and then in turn oxidized to the ferric condition at the positive plate, and also to some extent by the air.

Effect on Positive Plates.—When iron in the ferrous condition is added to the solution it is oxidized by the active material of the positive plates to ferric sulphate, accompanied by the formation of lead sulphate and water. Assuming the following equation for the reaction:

$$PbO_2+2FeSO_4+2H_2SO_4 \rightarrow PbSO_4+Fe_2(SO_4)_3+2H_2O \quad . \quad (1)$$

The lead sulphate which is formed permits an accurate calculation to be made of the extent of the reaction from the gain in weight of the plates. The gain in weight of the positive plates must, however, be calculated as $PbSO_4 : (PbSO_4-PbO_2)$, because the plate gains the sulphate radical SO_4 as the result of the reaction but loses simultaneously two oxygen atoms for each molecule of lead sulphate which is formed. The reaction expressed by Equation (1) proceeds to completion if sufficient time is allowed. That is to say, all of the ferrous sulphate is oxidized to the ferric condition, and beyond this point the rate of formation of lead sulphate is essentially the same as for plates in pure acid solutions. The results of these experiments showed that the curves representing data obtained from the iron solutions become parallel to those for the pure acid solutions after about 150 hours. We may, therefore, calculate the amount of lead sulphate which should be formed and compare it with the amount determined by the weighings. Such a comparison is made in Table XXI.

TABLE XXI

COMPARISON OF CALCULATED AND OBSERVED VALUES FOR POSITIVE PLATES IN SOLUTIONS CONTAINING IRON

Amount of Iron Added		Equivalent Ferrous Sulphate, Grams	Calculated Equivalent Lead Sulphate, Grams	Observed Amount of Lead Sulphate, Grams
Per Cent	Grams			
0.4	22.5	61.2	61.2	60.2
0.08	4.5	12.2	12.2	11.8
0.012	0.675	2.7	2.7	3.4

Since the reaction expressed in Equation (1) came to a definite termination, this afforded an excellent opportunity to determine what the effect of introducing negative plates into the solution would be. This case represents the condition of a battery containing both positive and negative plates. One charged negative plate was immersed in each solution at the conclusion of 360 hours. These plates were not in electrical contact with the positive plates. The reduction of the iron to the ferrous condition began immediately and the product in turn was reoxidized by the positive plates, accompanied by a further discharge. Curves showing the observations which were made are given in Fig. 45, the experiment being continued until 820 hours had elapsed. Iron has a destructive corroding action on the positive plates, particularly those of the Planté variety, because it increases the rate of sulphation.

Effect on Negative Plates.—The action of iron on the negative plates is much more pronounced than on the positives, and the local action produced is in excess of the amount which would be calculated from the reduction of the ferric sulphate. The effect is probably the result of two simultaneous reactions, which may be represented by the following equations:

$$Pb + Fe_2(SO_4)_3 \rightarrow PbSO_4 + 2FeSO_4 \quad . \quad . \quad . \quad . \quad (2a)$$

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2 \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

The amounts of iron added to the solutions were 4.5 grams and 0.675 gram. These are equivalent to 16.1 grams and 2.4 grams of ferric sulphate. On the basis of Equation (2*a*) these amounts will account for 13.4 and 2.0 grams of lead sulphate, respectively.

The curves, Fig. 46, show the gain in weight of the plates in terms of the sulphate, SO_4, taken from the electrolyte. This gain in weight

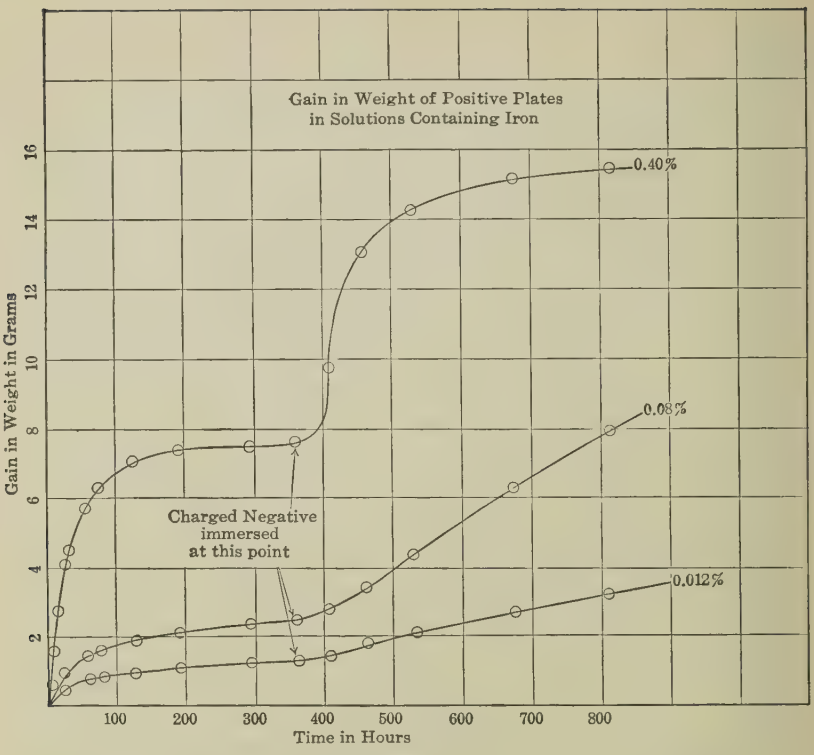

FIG. 45.—Effect of iron in producing local action at the positive plate.

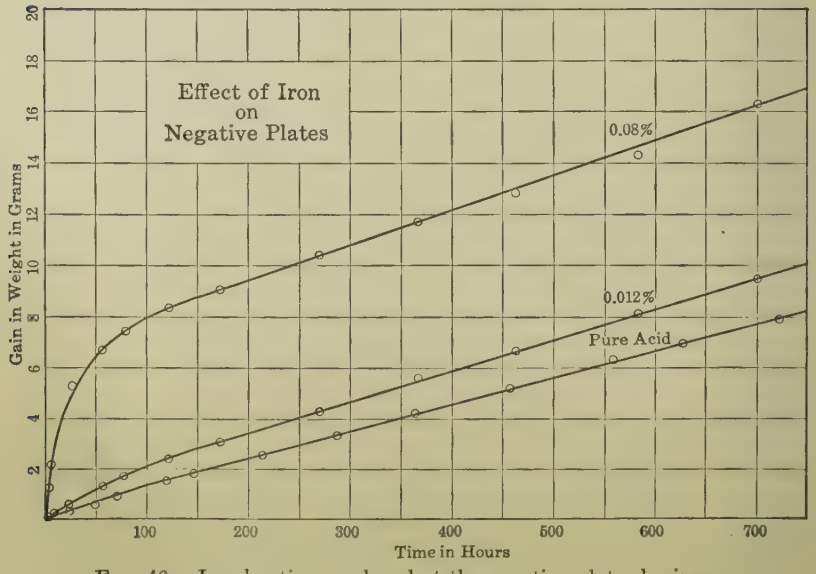

FIG. 46.—Local action produced at the negative plates by iron.

calculated to lead sulphate, $PbSO_4$, is greatly in excess of what may be accounted for by the reduction of the iron salt from the ferric to the ferrous condition. The curves show also that the gain in weight of the plates in the solutions to which iron had been added is in excess of the sulphation of similar plates in the pure acid. This indicates clearly that the presence of iron accelerates the reaction between sulphuric acid and lead, as represented by Equation (2*b*).

In the early stages of the experiment, when considerable ferric iron was present, this reaction was greatly accelerated, as shown by the rapid rise in the curves. When 150 hours had elapsed, this accelerating effect of the iron seems to have died out.

After 150 hours the curves shown in Fig. 46 are all approximately straight, but they diverge slightly, which shows that sulphate was being formed at a slightly greater rate on the plates in the solutions to which iron was added than in the pure acid. This effect is probably to be accounted for by the well-known slow spontaneous reoxidation of the ferrous sulphate by the air and its subsequent reduction by the negative plates during the long time that the experiment lasted.

Effect of Manganese on Negative Plates.—The experimental results obtained when negative plates were immersed in solutions containing manganese are shown in Fig. 47. The lowest curve represents the sulphation of the plates in pure acid solutions. The three curves above this are for similar solutions to which were added, respectively, 0.04 per cent, 0.08 per cent, and 0.40 per cent of manganese as potassium permanganate.

It is at once apparent that the effects produced are not proportional to the amounts of manganese added. The reason for this is a reaction between the sulphuric acid and the potassium permanganate, which is independent of the reaction at the plates. The reaction between the permanganate and the 1.250 sp. gr. acid may be expressed by the equation:

$$4KMnO_4 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2 \quad . \quad (3)$$

This is a slow reaction that may be demonstrated by a simple laboratory test, several hours being required to collect enough of the oxygen to make a satisfactory test. During the experiments the gas (oxygen) given off appeared in small amounts over the entire surface of the liquid. It was not localized at the plates.

The reactions which take place at the plates, in contradistinction to the above reaction, which occurs whether the plates are present or not, results in decolorizing the permanganate and in the formation of lead sulphate and manganese dioxide. The reactions are not fully

understood, but the following equation, which is in accordance with the observed facts, is believed to represent the reaction:

$$2KMnO_4+4H_2SO_4+3Pb \rightarrow K_2SO_4+2MnO_2+3PbSO_4+4H_2O. \quad (4)$$

There are probably several intermediate reactions which take place before the end products are reached. A sludge which fell to the bottom

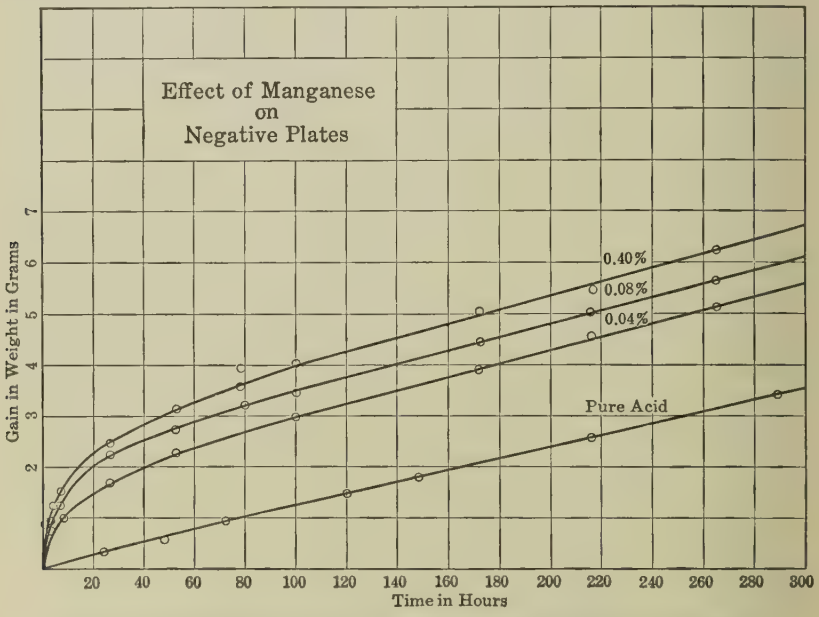

FIG. 47.—Local action produced at the negative plates by manganese.

of the jar was tested and found to be hydrated manganese dioxide. Possibly some of the manganese was converted into manganese sulphate. No gassing was visible at the plates.

Positives in Solutions Containing Manganese.—The manganese was added to the solutions as manganous sulphate, $MnSO_4$. The solutions were initially colorless, but began to show a purple coloration almost immediately after the positive plates were immersed. This indicates the formation of permanganic acid, $HMnO_4$, probably according to the equation:

$$5PbO_2+2MnSO_4+3H_2SO_4 \rightarrow 2HMnO_4+5PbSO_4+2H_2O \ . \quad (5)$$

The solutions containing 0.4 per cent of manganese became so dark

within one hour after the plates were immersed that the plates were no longer visible.

A rapid gain in weight of the plates was observed, as shown in Fig. 48. Comparing the results for both positives and negatives obtained in solutions with 0.08 per cent of manganese, it was found that the gain of the positives was much larger as a result of the oxidation of the manganous sulphate than the gain of the negatives resulting from the reduction of permanganate in the same length of time. After the

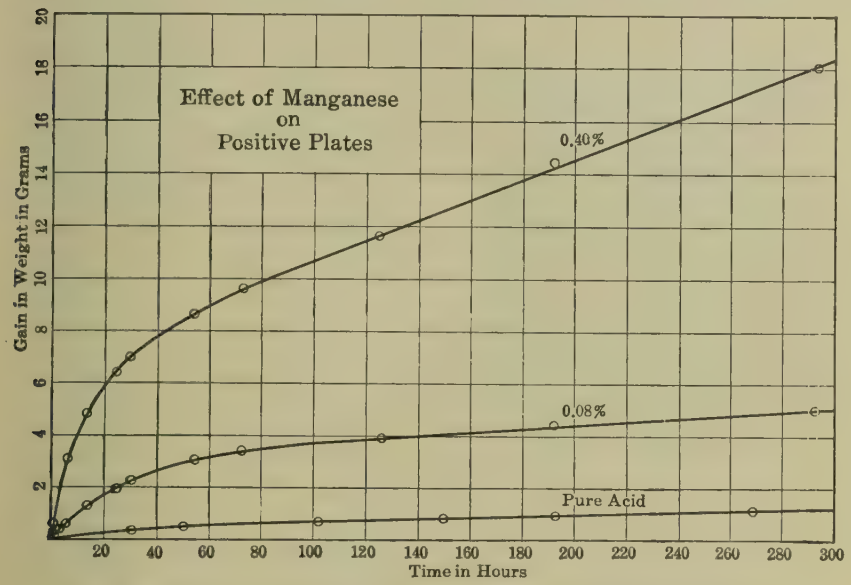

FIG. 48.—Local action produced at the positive plates by manganese.

rapid gain during the first fifty hours, the plates continued to gain in weight at a rate somewhat more rapid than for similar plates in the pure acid solution. The rate of the gain, however, steadily decreased, indicating that the reactions were becoming complete.

A deposit was formed on the plates, on the sides of the glass jar, and to some extent on the surface of the liquid. The deposit on the plates after drying was a dull, sooty black which filled the pores of the plates, the excess forming a rough, spongy layer over most of the plate surface also. One plate is shown in Fig. 49. Chemical analysis showed that this deposit was manganese dioxide, MnO_2. It seems probable that the gain in weight of the plates during the first period of perhaps fifty hours is largely the lead sulphate formed as a result of oxidizing the manganous sulphate, but an important part of the total gain in

weight is due to manganese dioxide deposited in the pores and on the surface of the plate.

Since the tendency of the negative plates is to throw the manganese out as a sludge, it might appear that the effects of manganese would gradually disappear. This, however, is not the case. The reason for the destructive effects of manganese are to be found in the reactions at the positive plates.

The manganese dioxide deposited upon the positive plates fills the pores of the active material and covers the plate with a hard, non-conducting film in a highly oxidized state. Two of the plates, a positive and a negative, upon which weighings had been made, were immersed in pure acid solution of specific gravity 1.250, and a charging current was passed through them, beginning with a rate somewhat below the normal finishing rate of charge. The positive began to gas immediately. Raising the charging rate to the normal value increased the gassing, and the electrolyte, initially clear, began to show a purple coloration indicating the re-formation of permanganic acid. The reaction at the positive during charge might be expressed by the equation:

FIG. 49.—Positive plate, showing a deposit of manganese dioxide.

$$2MnO_2+3O+H_2O \rightarrow 2HMnO_4 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This reaction at the positive occurred more rapidly than the reduction at the negative, as shown by the increasing coloration of the electrolyte due to permanganic acid. With the re-formation of permanganic acid by the charging process, the battery is again put in condition for a repetition of the reactions represented by Equation (5). It should be noted that the equation for charging makes no provision for the oxidation of the lead sulphate at the positive plate. Plates that are heavily coated with MnO_2 can receive but little charge. The pores are stopped and part of the energy is expended in the reaction on the manganese dioxide and part in the liberation of excess oxygen which normally would oxidize the lead sulphate.

Effect of Other Impurities.—There are a considerable number of other metals, besides copper and platinum, which are more noble

than lead and therefore deposit on the negative plates. These include tin, antimony, arsenic, mercury, silver, palladium, gold, and tungsten. Not all of these produce serious effects. The determining factor which differentiates the harmful from the harmless impurities appears to be the readiness with which hydrogen can be discharged upon the surface of the impurity. When one of these impurities is deposited upon the negative plate, it forms a galvanic couple with the underlying lead, as was the case when platinum was present. The impurity is the cathode, and hydrogen must discharge at this point, if local action is to take place. An excess voltage over that for reversible reactions, the so-called over-voltage, is required for the deposition of hydrogen on the surface of the various metals. The over-voltage is least for platinum and gold, and considerably more for copper and silver, from which it follows that platinum is a much worse impurity than copper, as the results given above have shown to be the case. Metals whose over-voltage exceeds the potential difference of sponge lead, measured against a normal hydrogen electrode, do not permit the liberation of hydrogen and therefore are not harmful. Kugel[11] has studied the effects of mercury, silver, copper, cadmium, arsenic, antimony, tin, bismuth, selenium, tellurium, vanadium, molybdenum, and tungsten. While none of these singly produced serious gas evolution at the negative plates, combinations of two or more in some cases produced very considerable reactions. Copper and tungsten in combination produced a rapid discharge of the cell. Further experiments along this line have been made by Scarpa.[12]

Injury to the plates of lead storage cells may be caused by the presence of nitric, hydrochloric, and acetic acids. These attack the metallic lead and the lead-antimony alloy forming the grids. In some cases, however, they tend to eliminate themselves, as, for example, nitric acid, part of which is liberated by the cell as oxides of nitrogen and the remainder reduced to ammonium sulphate in the electrolyte. Nitric acid is a solvent for lead and it exerts a strong forming tendency on the positive plate. Its chief action on the pasted plate, however, is to attack the material of the grid. Hydrochloric is similar to nitric acid in its property of being a solvent for lead. Hydrochloric acid attacks both the sponge lead of the negative plate and the lead peroxide of the positive plate. Chlorine gas is liberated during charging at the latter, while a portion of the chlorine is oxidized to perchloric acid and remains in the electrolyte. Acetic acid attacks the positive plate primarily, but is gradually decomposed by the charging current and escapes as carbon dioxide. Organic

[11] Elektrotech. Zeitschr., 13, pp. 8 and 19, 1892.

[12] L'Elettrotecnica, 6, p. 317, 1919.

substances which may be present in the electrolyte generally attack the grids of the positive plates, if they exert any deleterious effect on the cell at all.

Ammonia may be present in the electrolyte as a result of absorption of the ammonia gas by the electrolyte, or it may come from the use of ammonium sulphate in preparing the paste for pasted plates, or from the reduction of nitric acid. It exerts some forming action on the positive plate and has been said to be a cause of self-discharge of both positive and negative plates. Tests have shown, however, that ammonia may be present in the electrolyte to the extent of even 50 parts in 100,000 without the battery losing more than 8 per cent in capacity while standing during a period of four weeks following full charge.

A series of tests by Helen Gillette [13] was made to determine the effect of various impurities on the self-discharge and life of storage batteries. The results of her experiments were as given in Table XXII. She found that the effects of most metals other than platinum wore off in time, and she ascribed this effect to the alloying of them with the underlying lead and the fact that they are gradually plated over with lead as the operation of the cell progresses.

Some local action is produced by the gases, oxygen and hydrogen, which are produced when the cells are on charge. The oxygen oxidizes the active materials of the negative plate, and the hydrogen reduces some of the lead peroxide of the positive plate. The extent of the reaction caused by these gases, when the electrolyte is saturated with them at the end of a charge, is small as compared with the total capacity of the battery, but probably accounts in part at least for the fact that the most rapid rate of loss of charge is observed immediately after the charging period.

The loss of capacity of a battery in service condition should average not more than 1 per cent per day. Specifications for starting and lighting batteries, as adopted by the Motor Transport Division of the Army, specify the maximum permissible loss during a period of four weeks as 30 per cent. Actual tests on batteries of this type have given results ranging all the way from 6 per cent to 85 per cent loss in this period. The lower the specific gravity of the electrolyte, the lower should be the rate of loss of charge. Batteries with Planté plates are subject to a more rapid loss of charge than is observed with pasted plates, because of the thin layer of peroxide in intimate contact with the lead of the plate itself.

The experiments of other investigators have shown that the presence of minute traces of antimony in the active material of the negative plates

[13] Trans. Amer. Electrochem. Soc., 41, p. 217, 1922.

produces more serious local action at the negative plates than the results given in Table XXII would indicate.

TABLE XXII

EFFECT OF IMPURITIES IN THE ELECTROLYTE ON THE SELF-DISCHARGE AND LIFE OF STORAGE BATTERIES

	Minimum Percentage which Produced Injury		Maximum Percentage which Produced No Injury	
	Self-discharge	Life	Self-discharge	Life
Magnesium	....	0.5	0.5	0.05
Manganese	0.005	0.005	....	....
Zinc	....	....	0.5	0.5
Cadmium	....	0.5	0.5	0.05
Iron	....	0.1	0.1	0.05
Nickel	....	....	0.5	0.5
Tin	....	....	0.5	0.5
Arsenic	0.5	....	0.05	0.5
Antimony	0.5	0.5	0.05	0.05
Mercury	....	0.5	0.5	0.05
Silver	0.1	....	0.05	0.5
Platinum	Not tested	0.00001	....	....
Hydrochloric acid	Not tested	0.5	Not tested	0.1
Nitric acid	5.00	....	1.0	1.0
Acetic acid	Not tested	5.0	Not tested	1.0

Specifications for sulphuric acid, both in the concentrated form and when diluted for use in storage batteries, differ very greatly as to the amount of the various impurities which are considered allowable. In Table XXIII are given the figures which are believed to be in accord with good commercial practice. If the amount of the impurities allowed by specifications is made too small, a serious difficulty may arise in finding acid sufficiently pure to meet them. On the other hand, the specifications must limit the impurities to such amounts as are still within the limits for satisfactory operation of the batteries. The table shows the maximum quantities of impurities which may be present in the concentrated sulphuric acid, in the electrolyte diluted for use in storage batteries, and in the electrolyte which may be withdrawn from batteries in actual use.

TABLE XXIII

PURITY OF SULPHURIC ACID AND SOLUTIONS FOR BATTERY USE

	Concentrated Acid	Unused Electrolyte	Used Electrolyte
Specific gravity 60° F.	1.835	1.280	1.280
Per cent H_2SO_4	93.19%	36.8%	36.8%
Color	Colorless	Colorless	Colorless
Suspended matter	None	None	Lead compounds only
Platinum	None	None	None
Arsenic and antimony	Traces	Traces	Traces
Manganese	Trace	Trace	Trace
Iron	0.010%	0.004%	0.015%
Copper	0 005%	0.002%	0.005%
Nitrates and nitrites	Traces	Traces	Traces
Chlorides calculated as Cl	Trace	Trace	Trace
Organic matter	Trace	Trace	Trace
Sulphurous acid	Trace	Trace	None

c. The Reduction of Sulphation.

Frequent attempts have been made to reduce the sulphating action of sulphuric acid on the plates of storage batteries by the addition of various substances. Chief among these has been sodium sulphate, which is frequently sold under the name of Glauber salts. Schoop,[14] as far back as 1895, expressed the opinion that the use of sodium sulphate was not beneficial. Its use appears to have originated with some experiments made in England by Preece. Neither is sodium sulphate a satisfactory substance for the removal of the sulphation from the plates. For this purpose Schoop advocates the use of sodium bisulphate, $NaHSO_4$, in place of the acid solution. When this is used, the acid electrolyte is poured out from the battery before the sodium bisulphate solution is added. It has been found possible in some cases, however, to simplify this treatment for the removal of sulphation by merely pouring out the acid electrolyte and filling the cells with distilled water. The cells are then put on charge at the normal rate, provided they do not gas excessively, or at a current density which will maintain the voltage at the terminals of the cell at approximately 2.3 volts. If low-current densities are used, considerably more time is required for the reduction of the lead sulphate. High-current densities, on the

[14] Das Sekundar Element, Encyklopädie der Electrochemie, IV, Part 2, p. 133, 1895.

other hand, raise the temperature of the cell, particularly when the internal resistance is high, because of the presence of lead sulphate; they may also result in hard gassing. A constant potential charge at 2.3 volts per cell, on the other hand, makes possible the maximum rate of progress. Current is delivered to the cell as rapidly as the chemical reactions can proceed. The temperature will not become excessive and the charging of the cell may be made automatic. While the water treatment may not be the best in all cases, it has been found satisfactory, particularly in the case of some batteries of the starting and lighting type.

d. Solid Electrolytes.

Various attempts have been made to solidify the electrolyte in storage cells in order to eliminate spilling, and for other reasons. Materials which have been used in the past for making the electrolyte viscous have included albumen, starch, burnt clay, pumice, cellulose, soap, fatty acids, plaster of Paris, asbestos, sand, water glass, and fullers' earth. Of these various substances, water glass is perhaps the most suitable. The solidification of the electrolyte is brought about by the formation of silicic acid, which may be either of sodium or potassium according to the composition of the water glass, sodium silicate being the more common. The reaction for the silicate and sulphuric acid may be represented by the following formula:

$$Na_2SiO_3 + xH_2O + H_2SO_4 \rightarrow SiO_2 \cdot (x+1)H_2O + Na_2SO_4$$

It is necessary that both the acid and the water glass should be pure. Chlorides are perhaps the most common impurity occurring in the water glass. The time of setting before solidification takes place, and the stiffness of the jelly afterwards, are regulated by the proportions of the acid and the water glass. When thickening of the mixture begins, the final setting process occurs within a very few minutes. This mixture represents an interesting time reaction. If the mixture is made from dilute solutions, as, for example, sulphuric acid of specific gravity 1.275 and water glass of specific gravity 1.210, the greater the percentage of water glass in proportion to the acid, the more quickly the jelly sets and the more solid it becomes. The hard jellies are resonant.

Jelly electrolytes may be made from mixtures of concentrated sulphuric acid and dilute solutions of water glass or from dilute solutions of the acid and somewhat more concentrated solutions of the water glass. The time of setting is shortened by increasing the percentage of water glass and by using stronger acid, but if the percentage of

water glass is too great crystals will form as soon as the two liquids are poured together and these crystals will make the jelly cloudy and granular. It is possible to prepare the jelly as a clear, translucent, bluish mass which varies in consistency from a thick liquid to a fairly hard, resonant solid. The time of setting for various combinations is shown in Fig. 50. The curves are numbered from 1 to 11 and represent different proportions of the water glass and acid solutions measured by volume. These are as follows:

Curve 1, 5 parts 1.275 acid to 1 part of water glass
" 2, 4 " 1.275 " 1 " "
" 3, 3 " 1.275 " 1 " "
" 4, 2 " 1.275 " 1 " "

Curve 5, 5 parts 1.400 acid to 1 part of water glass
" 6, 4 " 1.400 " 1 " "
" 7, 3 " 1.400 " 1 " "
" 8, 2 " 1.400 " 1 " "

Curve 9, 1 part 1.84 acid to 4 parts of water glass
" 10, 1 " 1.84 " 3 " "
" 11, 1 " 1.84 " 2 " "

Batteries containing jelly electrolytes do not have as good electrical properties as those with the ordinary electrolytes. The internal resistance is higher and the capacity lower. They do not last well in service; and in spite of the many attempts to use this material, no battery of which the author has knowledge has stood the test of time. Comparisons of a starting and lighting battery containing a jelly electrolyte, with the minimum required capacity for the same size of battery, as listed in the Motor Transport Division of the Army specifications, gave the following results:

Rate of Discharge	Minimum Required Capacity	Measured Capacity of Battery with Jelly
5-hour	60	47
20-minute	31	11

The deficient capacity of the battery with the jelly electrolyte is apparent. It is also of interest to note the change in capacity of the battery, which was a new one, with succeeding discharges. The capacity decreased during 7 cycles by 14 per cent, although a new battery ordinarily gains during this stage of its life history.

Since the jelly formed by the action of the water glass and the acid has a tendency to crack away from the plates of the storage battery,

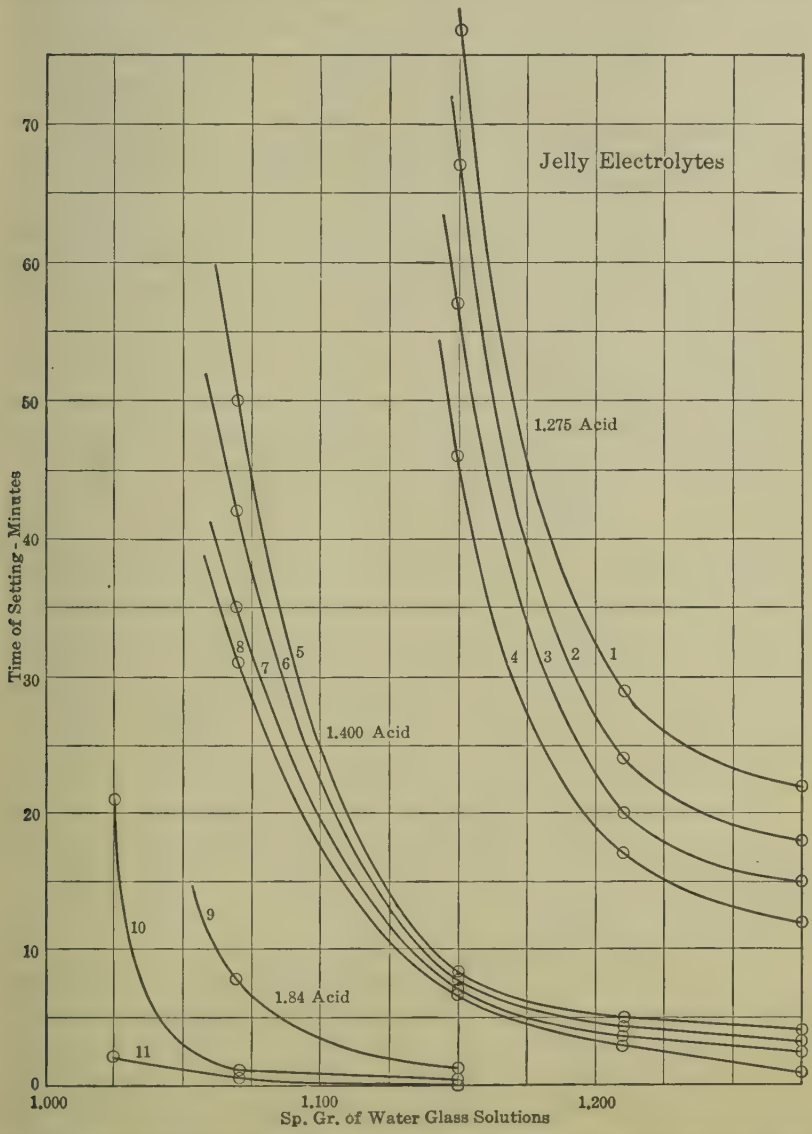

FIG. 50.—Preparation of jelly electrolytes from solutions of sulphuric acid and water glass.

owing to shrinkage occurring because of the evaporation of water, Schoop [15] has advocated the addition of paper stock, cellulose, or

[15] Loc. cit., p. 140.

asbestos to the mixture to serve as a binder. In preparing this material for use, the water glass is poured into the acid and thoroughly mixed. The binding material is then added, and the mixture allowed to stand until thickening of the solution is observable. When this point comes, it is necessary to pour the electrolyte into the cells immediately, as it is impossible to do so after solidification has actually taken place. When the electrolyte is prepared in this manner, it will not stick to the plates. Gas bubbles, which are formed at the plates during the process of the charging, will have an opportunity to escape between the plate and the layer of solid electrolyte. A layer of fluid electrolyte is desirable between the solid electrolyte and the surface of the plate. This facilitates the reactions within the storage battery and increases the capacity. Schoop obtained a patent [16] on jelly electrolytes in 1889. His experiments were further described in 1890.[17]

The resistance of a solid electrolyte of this character is approximately double that of the ordinary liquid electrolyte. Local action is considerably increased and the capacity of the cells reduced. The use of such electrolytes may be found desirable for special work, but has not found favor for the ordinary types of service. The use of sodium silicate for the preparation of solid electrolytes has been periodically rediscovered a number of times during recent years. Its use, however, dates back probably thirty years. A clear and detailed description of its preparation has been given by Schoop in the reference previously referred to.

Storage batteries containing plaster of Paris, fullers' earth, and similar substances have also appeared from time to time. These in general give small capacity in proportion to the size and weight of the batteries. It has been shown that in some cases the capacity is less than half of what would be expected from a battery of the same size containing normal electrolyte.

e. "Patent" Electrolytes.

Within the past few years, a considerable number of special electrolytes for use in storage cells, particularly of the starting and lighting type, have appeared. For the lack of a better designation for these electrolytes, they have been commonly referred to as patent electrolytes. Very few of them, however, are patented, and for the most part their composition is not revealed by the manufacturers. From the tests and experiments which have been made on this class of substances it may be stated that few, if any, of them have any real merit. They fall

[16] Electrotech. Zeit., 10, p. 473, 1889.

[17] Electrician, 25, p. 253, 1890.

naturally into three classes, the first of which includes those consisting merely of ordinary sulphuric-acid solution, of approximately customary densities, sold under trade names at fancy prices and with extravagant claims. The second class of these electrolytes contains substances, such as sodium sulphates, which are supposed to decrease the sulphation of the plates within the battery. The third class is that containing the addition of various corrosive agents to the sulphuric acid. These include bichromates, nitrates, and similar substances.

One of the most common claims made for electrolytes of this type is that the electrolyte is capable of charging the battery within a very short period of time or in a few minutes. It is sometimes stated that the electrolyte is "charged." This is obviously not the case. It is true that any battery may be partially charged by an electric current within a few minutes, but by the term charged we generally understand that the battery is fully charged. It is obviously impossible that the battery should be charged instantaneously or in a short time. The reactions taking place within the battery are in accordance with Faraday's law, irrespective of the particular substances which the electrolytes may contain.

If the electrolyte be poured out of a discharged battery and a more concentrated electrolyte then added, a small additional capacity may be obtained from the remaining active materials of the plates, and so, in the absence of exact measurements, the battery may appear to be charged; but the addition of a strong electrolyte to obtain a little more capacity is analogous to beating an exhausted horse.

7. PROPERTIES OF ALKALINE ELECTROLYTES

The electrolyte for the alkaline storage batteries, in which the electrodes are nickel oxide and iron, is a solution of potassium hydroxide in water. To this solution, as used in the Edison batteries, is added a small amount of lithium hydroxide. The lithium hydroxide has a beneficial effect on the operation of the cells, but is not necessary for the fundamental reactions which occur. The use of the lithium hydroxide is based on the results of experiment rather than on theoretical considerations. Edison has stated that the lithia, unlike sodium or potassium, migrates to the anode during charge, so that when an Edison battery is fully charged most of the lithia is in the nickel tubes in some obscure combination, but on discharge this combination is broken up and the lithia is outside. The lithia is considered essential for long life of the Edison battery, since a new battery without it has a falling life

curve, but when the lithia is present the curve rises slowly for a considerable time before it begins to fall.

The concentration and chemical composition of the alkaline electrolytes, considered as a whole, do not change during the periods of charge and discharge. The measurement of the specific gravity is, therefore, of less importance than for sulphuric-acid electrolyte used in the lead batteries. Occasional measurements of the specific gravity should be made, however, because there is a gradual weakening of the electrolyte, accompanied by a decrease in capacity of the battery to the point at which renewal is required.

The alkaline electrolytes for Edison cells are distinguished as "First Fill Electrolyte," "Refill Electrolyte," and "Renewal Electrolyte." The first is a 21 per cent solution of potassium hydroxide in water with 50 grams of lithium hydroxide to the liter of solution. The second is also a 21 per cent solution of potassium hydroxide with x [18] grams of lithium hydroxide. The last is a 25 per cent solution of potassium hydroxide with 15 grams of lithium hydroxide per liter. The uses of these solutions are indicated, in a general way, by their names. The initial filling of the cells at the factory is done with the "First Fill Electrolyte" with extra dry lithium hydroxide added according to the type of cell, to provide the correct amount per unit of the positive active material. The second kind of electrolyte is used mostly in export batteries, which after formation are shipped "dead" electrolytically and dry. The refill electrolyte is also used to replace losses caused by spillage, or when it is necessary to replace the electrolyte because of impurities. The third or "Renewal" electrolyte is used when the previous solution has reached the low limit of specific gravity. It is more concentrated than the first fill, in order to compensate for the dilution caused by the original electrolyte held in the pores of the plates.

Before these electrolytes are placed in the cells, the normal specific gravities are as follows:

	Potassium Solutions, Sp. Gr. at 60° F.	Soda Solutions, Sp. Gr. at 60° F.
First-fill electrolyte	1.228 to 1.230	1.195 to 1.200
Refill electrolyte	1.210 to 1.215	1.183 to 1.186
Renewal electrolyte	1.248 to 1.250	1.188 to 1.195

[18] The amount of lithia is made approximately equal to the quantity found after formation in the original electrolyte.

When the electrolyte has decreased in the course of service to a specific gravity of 1.160 (sodium electrolytes 1.130), it should be renewed. In determining when this limiting value is reached, certain precautions must be taken. The electrolyte must be adjusted to the proper level and thoroughly mixed by giving the battery a full charge, and the sample which is taken must be free from gas bubbles at the time that the specific gravity is measured. Correction must be made for temperature if the measurements are made at other than the standard temperature of 60° F. Normally the electrolyte will require renewal two or three times during the useful life of the battery. Operating a battery containing electrolyte of lower specific gravity than the limits mentioned above will produce sluggishness, loss of capacity, and rapid breakdown in heavy service. Since these difficulties may also be caused by the presence of impurities in the electrolyte, a chemical analysis of the electrolyte or the water used for flushing the cells may sometimes be necessary.

Sufficient renewal electrolyte should be procured when the results of careful measurements indicate that renewal is necessary. When it is available, the battery should be discharged at the normal rate to zero voltage and then short-circuited for one hour. The old electrolyte is to be poured out while the battery is vigorously shaken to rinse the plates. It may be necessary to handle the cells separately, if they are large. Water should not be used for rinsing the plates. When each cell is empty, the new electrolyte should be added immediately, and when all are filled the battery should be put on charge at the normal rate for several hours longer than the usual charging period. During this operation observations of the temperature ought to be made at intervals, and if the battery should reach the limits set for normal operation (p. 226) the charge should be interrupted until the battery has cooled.

Potassium hydroxide is variously called potassium hydrate, caustic potash, and potassa. It is a white solid substance which is very deliquescent and easily soluble in water. It dissolves the skin and many organic substances. Potassium hydroxide, both in the solid state and in solution, absorbs carbon dioxide from the air. It is necessary to protect the solution in the battery, by gas valves in the vent plugs, from contamination by carbon dioxide. These valves are designed to prevent the ingress of gas, but to permit the ready escape of gas generated within the cell. Potassium hydroxide may be prepared electrolytically from potassium chloride. The properties and preparation of sodium hydroxide are similar to those of potassium hydroxide. Lithium hydroxide is obtained in solution by the action of lime on a solution of lithium car-

bonate. It is a bluish liquid and is very caustic. Crystals of lithium hydrate contain only 54 per cent lithium hydroxide as compared with 85 per cent potassium hydroxide and 98 per cent sodium hydroxide in these other hydroxides.

a. Density and Percentage Strength of the Solutions.

The data which are given in Table XXIV are for pure solutions of potassium and sodium hydroxides without the addition of the lithium hydroxide. The amount of the latter which is added is relatively small and the electrolytes are, therefore, represented sufficiently well by the properties of the pure solutions for which accurate information is available. The percentage composition is given for densities at 18° C., since most of the original material is given on this basis. The change in density for solutions of sodium hydroxide calculated as the average per degree for the range 10° to 40° C. is also given in the table. To correct the observed results at any temperature within this range to the standard temperature, one unit in the third decimal place is to be added for each two degrees Centigrade or three degrees Fahrenheit if the temperature is above the standard temperature, or subtracted, if below it. These corrections are approximately the same as for the acid electrolyte used in the lead batteries. Although the figures for the effect of temperature

TABLE XXIV

Density and Percentage Composition of Solutions of Potassium and Sodium Hydroxide

Density $\frac{18° C.}{4° C.}$	Per Cent * KOH	Per Cent † NaOH	Change Density † per Degree, NaOH	
			° C.	° F.
1.050	5.6	4.6	0.00037	0.00020
1.100	10.9	9.2	0.00045	0.00025
1.150	16.1	13.7	0.00050	0.00028
1.200	21.1	18.2	0.00054	0.00030
1.250	26.0	22.7	0.00057	0.00032
1.300	30.8	27.3	0.00060	0.00033
1.350	35.3	32.0	0.00063	0.00035
1.400	39.8	37.0	0.00066	0.00037
1.450	44.0	42.0	0.00069	0.00038

* Calculated from the results of Kohlrausch, Wied. Ann. 6, p. 1, 1879.
† Calculated from the results of Bousfield and Lowry, Phil. Trans. 204, p. 253, 1905.

on the density of potassium hydroxide are not given, the corrections for the other may be applied for practical purposes.

For the same density of solution, the percentage of sodium hydroxide is less than for the potassium hydroxide. The electrolytes and renewal solutions used in the nickel-iron cells fall within the range of densities from 1.150 to 1.250. The density or specific gravity of the alkaline solutions should not be measured with the same hydrometer that is used for acid solutions, unless it is washed free from acid. Good practice requires a separate hydrometer for each kind of electrolyte.

b. Resistivity.

The resistivity of the alkaline electrolytes varies with the concentration, the temperature, and the amount of lithium hydroxide added to the solution. The electrical resistance depends on the resistivity, the length of the path, and the cross-sectional area through which the current flows, according to the equation $R = \rho \frac{l}{s}$ where R is the resistance, l the length, s the cross-section, and ρ the resistivity. The unit of resistivity is the ohm-centimeter, which was explained in connection with the resistivity of sulphuric-acid solutions on page 79. The resistivity of solutions of pure potassium and sodium hydroxides is given in Table XXV at 18° C. (64.4° F.). The resistivity of the solutions actually used is slightly higher than the figures given in the table, because of the addition of the lithium hydroxide. The percentage increase in the resistivity of a 21 per cent solution of potassium hydroxide containing 50 grams of lithium hydroxide per liter was determined by Turnock [19] to be 21 per cent. Smaller amounts produce effects shown in Table XXVI. The addition of the lithium hydrate increases the capacity of the cells, as stated on page 125, but it drives back the ionization of the potassium hydroxide according to the law of mass action, decreasing the conductivity of the solution. By plotting the results given in Table XXV, it will be seen that the shape of the resistivity-concentration curve for potassium electrolyte is better suited to storage battery uses than the curve for the sodium electrolyte. It is somewhat similar to the resistivity curve for sulphuric acid (Fig. 37), but the resistivity is higher. The sodium electrolyte has a higher resistivity than the potassium electrolyte for corresponding concentrations and can only be used over a narrow range of concentrations because the resistivity increases abruptly for the concentrations below 1.130 and above 1.170 sp. gr.

[19] Trans. Am. Electrochem. Soc., 32, p. 405, 1917.

TABLE XXV

RESISTIVITY OF SOLUTIONS OF POTASSIUM AND SODIUM HYDROXIDES

(The resistivities are expressed in ohm-centimeters, temperature 18° C.)

Density $\frac{18° C.}{4° C.}$	Resistivity * KOH	Resistivity † NaOH	Temperature Coefficient	
			KOH	NaOH
1.050	4.97	5.41	0.0186	0.0200
1.100	2.99	3.39	0.0187	0.0214
1.150	2.25	2.89	0.0192	0.0235
1.200	1.95	2.93	0.0198	0.0274
1.250	1.84	3.35	0.0208	0.0326
1.300	1.86	4.15	0.0222	0.0395
1.350	1.98	5.42	0.0242	0.0478
1.400	2.21	7.09	0.0268	0.0570
1.450	2.51	8.95	0.0296	0.0668

* Calculated from the results of Kohlrausch, Wied. Ann. 6, p. 145, 1879.
† Calculated from the results of Bousfield and Lowry, Phil. Trans. 204, p. 253, 1905.

TABLE XXVI

PERCENTAGE INCREASE IN RESISTIVITY OF 21 PER CENT SOLUTION OF POTASSIUM HYDROXIDE WITH LITHIUM HYDROXIDE ADDED

Grams of LiOH, per Liter	Per Cent Increase * in Resistivity
10	7.1
20	11.4
30	15.4
40	18.5
50	21.0

* Turnock, loc. cit.

The temperature coefficient of resistivity of solutions of sodium hydroxide is considerably more than for the solutions of potassium hydroxide of corresponding densities.

c. Freezing Points.

The freezing points of the electrolytes used in the nickel-iron batteries are given in Table XXVII.

TABLE XXVII

FREEZING-POINTS OF ELECTROLYTE USED IN ALKALINE STORAGE BATTERIES

Specific Gravity $\frac{15° \text{ C.}}{15° \text{ C.}}$	Potash Electrolyte		Soda Electrolyte	
	° C.	° F.	° C.	° F.
1.125	− 7	+19	− 8	+17
1.150	−11	+12	−12	+10
1.175	−15	+ 5	−16	+ 3
1.200	−21	− 6	−22	− 8
1.225	−28	−18	−29	−20

8. SHIPPING THE ELECTROLYTE

The electrolyte for storage batteries is classed as a corrosive liquid by the regulations[20] of the Interstate Commerce Commission. The regulations require compliance with certain rules relating to the containers, the method of packing, and the labels. Concentrated acid may be shipped in tank cars, drums, or carboys. The tank cars range in capacity from 60,000 to 160,000 pounds and are usually arranged with piping for blowing the acid out by compressed air. To avoid contamination of the acid by the iron, it is highly important that the acid be concentrated and that the tank be filled full and tightly sealed. Dilute acid, sometimes called "electrolyte," and ranging in specific gravity up to about 1.400, can be shipped only in glass carboys. The term "carboy" does not denote a container of definite capacity. The carboy is a glass bottle having a capacity of 10 to 13 gallons. Usually a carboy holds about 180 pounds of concentrated acid. The glass of the carboy is protected from breakage by a box packed with straw or other material.

The electrolyte for the nickel-iron batteries is shipped in steel containers. The smaller amounts, up to 22 pounds, are contained in cans similar to the containers for the cells. Larger amounts of 100 to 500 pounds are shipped in steel drums.

Rebates are usually allowed for the return of the drums and carboys when they are empty.

[20] Regulations for the Transportation of Explosives and Other Dangerous Articles by Freight and Express.

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CHAPTER IV

THEORY OF REACTIONS, ENERGY TRANSFORMATION, AND VOLTAGE

1. ELEMENTARY THEORY OF ELECTRIC CELLS

The simplest form of cell may be made of two strips of copper and zinc immersed in water acidulated with sulphuric acid. If the zinc is sufficiently pure to be free from local action, there will be no visible effect until the zinc and copper are connected by a wire. The strips are, however, at different potentials with respect to each other, and when they are connected by a wire a current of electricity will flow in the wire. As this action progresses the strip of zinc will pass into solution and bubbles of gas will form at the copper electrode and collect on its surface. This gas is hydrogen which is formed from the electrolyte. The electric current flows from the copper strip through the wire to the zinc strip, and from the zinc strip through the electrolyte to the copper.

As the action of this cell progresess, the sulphuric acid of the electrolyte is gradually replaced by zinc sulphate which is formed at the dissolving zinc electrode. This diminishes the voltage of the cell. A greater decrease, however, is caused by the collection of gas bubbles on the copper. Both effects produce "polarization." Such a cell is of little practical importance.

The Daniell cell, devised in 1836, is a modification of the foregoing and possesses important advantages since it eliminates the decrease in voltage caused by polarization. This cell consists of a strip of copper immersed in a solution of copper sulphate and a zinc strip in a solution of zinc sulphate, the two liquids being separated by a porous diaphragm to prevent mixing. As the action of this cell progresses the zinc electrode dissolves, forming more zinc sulphate, and the copper electrode is increased by the deposition of copper from the electrolyte. The Daniell cell will be referred to in the pages that follow, as occasion may require, since because of its relative simplicity as compared with other types it is useful in explaining parts of the theory.

a. Ions and Electrons.

The current is transported through the electrolyte by particles of molecular size that carry electrical charges. These are called " ions," a term that was originated by Faraday nearly a hundred years ago. The ions are formed from the electrodes or from the substance that is dissolved in water to make the electrolyte. When zinc sulphate, for example, is dissolved in water, a spontaneous decomposition of a certain proportion of the zinc-sulphate molecules takes place. The products are zinc ions and sulphate ions. This process is called " dissociation." The zinc sulphate in the molecular state is electrically neutral, but as the molecules dissociate, positive and negative charges in equivalent amounts appear on the ions. In general, the metallic ions and hydrogen ions carry the positive charges; the non-metallic elements and radicals carry the negative charges. The sign of the charges has been ascertained by the direction in which the various ions move when between electrodes of opposite polarity, as in a simple electrolytic cell.

It was found many years ago that ions of substances that are divalent carry twice the charge of the ions formed from monovalent substances. Trivalent and tetravalent ions have, respectively, three and four times the charge of the monovalent ions. Within recent years the electron theory has given an explanation of the magnitude of these charges.

The electron is conceived to be a discrete and definite charge of negative electricity within the atom, vitally affecting the different forms of matter in the physical states as we know them. Copper, lead, hydrogen, and the other elements differ from one another in atomic structure according to the number and motion of the electrons, which constitute something like a miniature solar system, within the atom. Some of the electrons are believed to move in orbits, from which no chemical or physical force now at our command can remove them. These are the inner electrons, as distinguished from the less stable, or valence, electrons, which may take part in the interchanges known as electrochemical reactions. The number of electrons that may take part in reactions fixes the valency. There is one electron for monovalent reactions, two for divalent reactions, and so on for trivalent and the higher valencies. As long as an element has its normal number of electrons it is electrically neutral, but if it loses one or more electrons it exhibits a positive charge equivalent in magnitude, but opposite in sign, to the negative charge or charges that it has lost. An atom or molecule thus becomes a positive ion. On the other hand, the gain of one or more electrons is manifested by negative charges. Since the electron is a definite quantity of electricity, it is easy to understand why the charges carried by the ions are simple multiples of a unit charge.

Recent researches have shown the relation between the electrons and the dissociation process, so that we may write an equation for the ionization of such a substance as zinc sulphate, as follows:

$$ZnSO_4 \leftrightarrows Zn^{++} + SO_4^{--}$$

The metallic ion, Zn^{++}, differs from the zinc atom both physically and chemically. Compared with an atom, it lacks two electrons; it is in solution; it moves under the influence of a potential gradient; and, finally, it has a marked tendency to attract and combine with oppositely charged ions. Probably the ions of opposite charges are combining and being formed continuously, but the proportion present at any time is determined by equilibrium conditions. A state of equilbrium is reached when the number forming during any specified interval of time is exactly equal to the number combining during the same interval. The equilibrium conditions which determine the proportion of the various ions present at any time depend on several factors. The nature of the dissolved substance and the solution pressure of the electrode (see p. 136) are of first importance. Some substances dissociate to a greater degree than others. The percentage of the molecules that dissociate also depends on the concentration of the solution. The more dilute the solution the greater will be the percentage dissociation, until 100 per cent, or complete dissociation, is reached; but this does not mean that more ions are present in dilute solutions than in those more concentrated. The presence of other dissolved substances and the flow of an electric current also affect the equilibrium condition.

Ions of the same kind are identical in their properties. No difference is observable between the zinc ions formed from a zinc electrode and those formed by the dissociation of zinc sulphate. The hydrogen ions in a storage battery all behave in the same way, irrespective of whether they came from dissociated molecules of water or sulphuric acid. The same is true of the lead ions, which can be derived from the lead sulphate or from the negative plate.

The motion of an electric charge constitutes an electric current. The motion of an ion in the electrolyte, or of an electron in a wire, is a transfer of a definite amount of electricity from one point to another. The actual amount of electricity transported by a single electron or ion is very small. Its value has been found to be

$$1.591 \times 10^{-19} \text{ coulomb.}$$

The number of ions required to transport one ampere flowing for one second (one coulomb) is, therefore, enormously great. It is preferable

to deal in magnitudes more easily comprehended. As a unit there has been chosen the aggregate charge carried by a number of ions equal in weight to the number of grams representing the atomic or molecular weight of the ion, which for convenience is designated as a "gram-ion." If the ion in question is monovalent, the total charge is 96,500 coulombs; if divalent, the charge is twice this amount, and so on. This is further discussed under Faraday's law on page 144.

In a storage battery there are many kinds of ions present to carry the current. The sulphuric acid dissociates by two steps into hydrogen ions H^+ and sulphate ions SO_4^{--}, there being twice as many of the former as of the latter. There may be also a few ions of the composition HSO_4^- from the initial step in the dissociation process. The water present contributes hydrogen ions, H^+, and hydroxyl ions, OH^-. A few lead ions, including both the divalent and the tetravalent states, are present. These are Pb^{++} and Pb^{++++}. According to some theories, there are also lead-peroxide ions, PbO_2^{--}. The lead and lead-peroxide ions are relatively unimportant in carrying the current because there are few of them, but they are of great importance in fixing the potential differences between the plates and the electrolytes, as will be shown.

The ions move quite independently of each other. Each has a definite amount of charge and moves with a speed characteristic of its kind when subjected to a specified potential gradient. The hydrogen ions move the fastest.

b. Potential Differences.

The differences of potential that exist between the electrodes and the electrolyte are conveniently explained by Nernst's conception of solution pressures. By this theory, it is assumed that all metals have a tendency to send their ions into solution, but it is observed that the metals which are easily oxidized, such as zinc or lead, have this tendency to a greater degree than gold or platinum which cannot be easily oxidized. Zinc and lead are therefore said to have greater solution pressures than gold or platinum. When a strip of zinc is immersed in a solution of zinc sulphate, as in the Daniell cell, zinc ions carrying positive charges are thrown into the solution. The strip of zinc becomes negatively charged because of an excess of electrons that remain after the departure of the positively charged ions from its surface. This reaction cannot continue indefinitely, since the positive charges of the ions in solution repel the positively charged ions leaving the surface of the zinc. The latter are also held back by the attraction of the negatively charged zinc strip. The magnitude of the charges on the strip of zinc and of the

surrounding electrolyte increases as more and more zinc ions are formed, until a state of equilibrium is eventually reached when the solution pressure of the metal is balanced by the electrostatic forces. This prevents the further formation of zinc ions. Figure 51 shows diagrammatically the double layer of charges. The ions which pass into the solution from the strip of zinc increase the osmotic pressure of the zinc ions which were formed from the zinc sulphate when it was dissolved in the water. As the tendency of the osmotic pressure is to deposit ions upon the strip of zinc as atoms of zinc, it is evident that the solution pressure of the zinc is opposed by the osmotic pressure of the zinc ions in the solution. When the solution pressure of the metal is

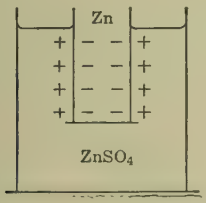

FIG. 51.—Zinc in a solution of zinc sulphate becomes negatively charged.

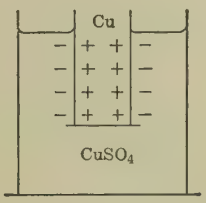

FIG. 52.—Copper in a solution of copper sulphate becomes positively charged.

equal to the osmotic pressure of the ions in solution, equilibrium is reached.

The copper electrode of the Daniell cell is immersed in a solution of copper sulphate. At this electrode the reaction produces a different result from that observed at the zinc electrode. The solution pressure of the copper is very small as compared with the osmotic pressure of the copper ions in the electrolyte. The result is a deposition of copper ions upon the surface of the strip of copper. When these ions are deposited their deficiency in electrons is imparted to the copper electrode. The electrode thereby acquires a positive charge, and the solution becomes negatively charged because of the excess of negative ions that remain. These negative ions are the sulphate ions that were formed by the dissociation of the copper sulphate. A double layer is again formed, as shown in Fig. 52. The equilibrium condition is reached when the electrostatic forces prevent the further deposition of copper ions on the electrode.

Other theories have been proposed to account for the potentials of the electrodes, and various objections have at times been raised to the theory of Nernst. Nernst's theory, however, gives a mental picture of

the process that is easily comprehended, and it has received wide acceptance.

c. The Convention as to Positive and Negative Potentials.

The result of practical importance that arises from the formation of the zinc ions at the zinc electrode and the deposition of copper ions at the copper electrode is the potential difference between the electrodes and the electrolyte. When the strip of zinc is immersed in a solution containing one gram-ionic weight of zinc ions, the electromotive force at the surface of contact between the solution and the zinc attains an equilibrium value of about 0.48 volt in a direction corresponding to the passage of current from the metal into the solution. The actual potential of the zinc with respect to the solution is negative. The copper, on the other hand, in a similar solution of copper ions, has a potential difference of 0.62 volt in a direction corresponding to the passage of the current from the solution to the metal. The copper is positive with respect to the solution. If a closed circuit between the zinc and the copper is formed, and at the same time the electrolytes are brought into contact through a porous diaphragm that will permit the passage of ions without allowing the two solutions to mix, a cell having a voltage equal to the algebraic difference of the potentials of the two electrodes with respect to the solution is formed. In the case of the Daniell cell, the combined voltage is $0.62-(-0.48)=1.10$ volts, neglecting the small potential difference that exists at the surface of contact between the solutions.

The polarity of the cell is defined by the polarity of the individual electrodes with respect to the electrolyte and, therefore, their potential relations to each other. In the Daniell cell the positive is the copper, although this is sometimes called the electronegative metal. Much confusion has arisen because of the lack of a standard terminology in this respect. The convention as here given has been adopted as standard by a number of organizations, including the American Electrochemical Society,[1] the International Congress of Pure and Applied Chemistry, 1922, and the Bureau of Standards. In dealing with the storage battery, in which the current flows in opposite directions when on charge and on discharge, there is further chance for confusion. Fortunately, however, the brown peroxide plates are so universally called the positives, and the gray, metallic sponge-lead plates, the negatives, that this terminology may be considered fully standardized. When the storage cell discharges, the peroxide plate is the positive in the same sense as the copper electrode of the Daniell cell.

[1] Trans. Am. Electrochem. Soc., 36, p. 3, 1919.

d. The Electrochemical Series.

An idea of the relative solution pressures of the various metals may be obtained from the potential differences between the electrodes and electrolytes containing one gram-ionic weight of the ions, which the metal discharges, per liter of solution; or, where it is not possible to measure the potentials directly, they may be computed from thermochemical data. A solution containing 96.07 grams of sulphate ions or 63.37 grams of zinc ions per liter of solution is said to contain a gram-ionic weight, or a "gram-ion," in each case. The elements that are easily oxidized are those that have the greatest tendency to send ions into the solution and are therefore the elements that are the most negative with respect to the solutions, because for every ion passing into the solution and carrying positive charges there is left behind an equivalent number of negative charges on the electrode. The more noble metals, on the other hand, have smaller solution pressures. Those which are observed to be positive with respect to the solution have the same tendency to send ions into the solution, but in this case the solution pressure is so small as to be overbalanced by the osmotic pressure of the ions already in solution. The result is that ions carrying positive charges deposit upon the surface of the electrode in excess of those thrown into solution and the electrode thereby acquires a positive charge. The magnitude of these solution pressures has been computed in some cases, but the figures surpass our power of comprehension. For example, the solution pressure (atmospheres) of potassium is about 6×10^{50}; of zinc, 1×10^{17}; of copper, 8×10^{-22}; and of platinum, 5×10^{-80}. It is better, therefore, to arrange the elements according to their potentials with respect to the electrolyte. The potentials are expressed in volts and are of magnitudes that are easily comprehended.

Lists of the elements arranged in the order of increasing potentials have been given by many authorities, but these differ somewhat both as to the order of the elements and the values assigned for their potentials. These differences are explainable in part by the various concentrations of the electrolytes which have been used. Some results are stated to be for normal solutions, others are for solutions containing an equivalent weight of the particular ion; but the more common method seems to be to express the concentrations in terms of gram-ions per liter. Such solutions are normal for the monovalent ions only. The potentials are measured against the normal hydrogen electrode or the normal calomel half-cell, both of which are described in Chapter V. The potentials may be expressed in terms of a scale based on either of these electrodes taken as zero, or in terms of the so-called absolute scale for which the hydrogen

electrode has a value +0.277 and the calomel cell a value +0.56. Potentials may be converted from one scale to another by the use of the following equation with careful attention to the algebraic signs of the quantities involved. E_a, E_h, and E_c are used to designate the potentials on the absolute, hydrogen, and calomel scales, respectively.

$$E_a = E_h + 0.277 = E_c + 0.56$$

A selected list of elements, with the approximate values of their potentials on the absolute scale, is given in Table XXVIII. The absolute scale has some advantages over the others for the present discussion. Metals following lead, such as copper, silver, and platinum, are the elements that deposit on the negative plates of storage batteries; but the elements that precede it will not be deposited under ordinary circumstances. The position of the various elements with reference

TABLE XXVIII

ELECTRODE POTENTIALS

(Calculated for electrochemical reactions of elements immersed in solutions containing 1 gram-ion per liter. The potentials are expressed as the potential of the electrode minus the potential of the solution on the so-called absolute scale for which the normal hydrogen electrode has the value +0.277 volt.)

Element	Valence	Potential in volts
Potassium	1	−2.6
Sodium	1	−2.4
Calcium	2	−2.3
Magnesium	2	−1.3
Manganese	2	−0.80
Zinc	2	−0.48
Iron	2	−0.15
Cadmium	2	−0.12
Nickel	2	+0.06
Lead	2	+0.16
Tin	2	+0.18
Iron	3	+0.24
Hydrogen	1	+0.277
Copper	2	+0.62
Antimony	3	+0.75
Copper	1	+0.79
Mercury	2	+1.08
Silver	1	+1.08
Platinum	4	+1.14
Gold	3	+1.36

to lead has a bearing on the effects they produce when present as impurities in the electrolyte. This is discussed in Chapter III.

A more complete list of the elements, showing the probable order in the electrochemical series, is as follows:

> Potassium, sodium, barium, strontium, calcium, magnesium, aluminum, manganese, zinc, iron, cadmium, cobalt, nickel, lead, tin, hydrogen, bismuth, copper, antimony, arsenic, mercury, silver, palladium, platinum, gold, silicon, tantalum, tellurium, carbon, boron, tungsten, molybdenum, vanadium, chromium, iodine, bromine, chlorine, fluorine, nitrogen, sulphur, oxygen.

In using the list of elements, the order cannot be considered to hold true in all cases. The order depends somewhat on the nature, concentration, and temperature of the solutions. Usually any metal will displace from solution the others which follow, and it will be displaced by those that preceded. Secondary reactions may interfere, however.

e. The Flow of Current.

When the terminals of a cell are connected through an external circuit by a wire, the current that flows is proportional to the potential difference of the electrodes and inversely proportional to the resistance of the whole circuit, including the resistance of the battery as well as that of the external circuit. This is in accordance with Ohm's law.

The Migration of Ions.—The flow of current is continuous throughout the entire circuit. The current in the wire is believed to consist of a stream of electrons flowing from the anode, negatively charged with respect to the solution, to the cathode. In the solution the current is carried by ions both positively and negatively charged, traveling in opposite directions to their respective electrodes. The positively charged ions, called "cations," move to the cathode which in the Daniell cell is the copper. The negatively charged ions, called the "anions," migrate to the anode. It is obvious that at the surface of the electrodes where one form of conduction meets the other, exchanges of electrons between the electrodes and the ions in the solution must take place, if the electric current is to flow continuously. The reactions which involve both the current carrying ions and electrons on the one hand and the chemical composition of the electrodes and electrolyte on the other are called electrochemical reactions.

Across any imaginary surface that may be drawn in the solution, the current is carried by the ions, each kind of ion carrying its propor-

tionate share. The ions that are the most numerous and travel the fastest carry a greater amount than the others, but all take part. At the electrodes, however, the actual transfer of current from the solution to the electrode is usually through the medium of only one kind of ion. Suppose that a zinc ion, having left the anode and traveled only part way to the cathode, meets and reacts with a sulphate ion that has traveled in the opposite direction, from the cathode. The ions neutralize each other and change into the molecular state, but the result is the transfer of two charges (the ions are divalent) from one electrode to the other. Few, if any, of the ions actually travel the entire distance from one electrode to the other.

To continue the relatively simple case of the Daniell cell for sake of illustration, it may be supposed that the solution pressure of the zinc driving the positively charged zinc ions into the solution leaves free negatively charged electrons which give to the zinc its negative charge. When a connection is made by a wire to the copper electrode, a path is provided for the electrons to flow to the positively charged copper. The motion of the electrons is opposite to the direction in which the current is said to flow. The departure of the electrons from the zinc disturbs the state of equilibrium between it and the electrolyte, and more zinc ions are thrown into the solution. Coincident with this, additional electrons are liberated in the zinc and they follow on through the wire after the others as long as the circuit remains closed. Two electrons, each with one negative charge, are freed, with the formation of each zinc ion. This process is represented by the ionic equation:

$$Zn - 2\ominus = Zn^{++} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The electrons, reaching the copper terminal after their passage through the wire, neutralize an equivalent number of positive charges, thereby disturbing the equilibrum of this electrode and permitting the further discharge of copper ions. Two electrons neutralize two positive charges and permit the deposit of one ion of copper, which gives up its charges. This fact is represented by the equation:

$$Cu^{++} + 2\ominus = Cu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The zinc cations move toward the cathode, carrying their share of the current through the electrolyte. Probably most of them combine with the sulphate anions moving in the opposite direction, to form zinc sulphate according to the equation:

$$Zn^{++} + SO_4^{--} = ZnSO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The relative motion of the electrons, anions, and cations is shown in Fig. 53.

In the solution around the cathode there are several different kinds of ions carrying positive charges and, therefore, several different reactions are possible. The transfer of positive charges is accomplished under ordinary circumstances, however, by the discharge of only one kind of ion. The factors which determine the preferential reaction are the relative electrolytic potentials and the relative concentrations of the ions. When each electron of the stream of electrons moving from the anode to the cathode through the wire reaches the cathode, it reduces the positive potential of the cathode by a small amount, and ions having

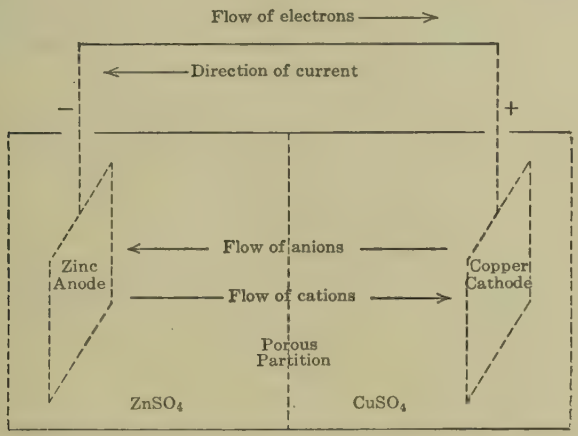

FIG. 53.—Relative flow of the ions, electrons, and the direction of the current in a Daniell cell.

the highest equilibrium potential, deposit. In the case of the Daniell cell these are the copper ions, Cu^{++}.

The unequal speeds of the ions produce concentration differences in the region of the electrodes, which have an important effect upon the performance of a battery. In a storage battery this effect is in addition to the actual consumption of the acid as it combines with the active materials of the plates when current is produced. During the discharge, hydrogen ions leave the region of the anode and migrate toward the cathode, while the sulphate ions go in the opposite direction. The speed of the hydrogen ions is greater than that of the sulphate ions, which is a fortunate circumstance in the operation of the lead storage battery, as otherwise the amount of acid required for the operation of the positive plate would be much larger than is actually the case.

Faraday's Law of Electrolysis.—In 1834 Faraday formulated his fundamental law of the relation between the amount of electrochemical action and the quantity of electricity passing through the cell. Many experiments since that time have proved the validity of this law, which is of the greatest importance in discussing the storage battery.

The first part of Faraday's law states that the chemical effects produced at the electrodes by the passage of an electric current are in direct proportion to the magnitude of the current and the time that it flows, that is, to the quantity of electricity. This law establishes a relationship between the output of a battery and the amount of active materials which it contains. It therefore denies the possibility of drawing current from the battery indefinitely (perpetual motion), or of charging it by merely changing the solution. Not all the materials within a battery may be used for the production of electric current, because of practical limitations, but interesting comparisons on the basis of Faraday's law may be made for the various types and kinds of batteries.

The second part of Faraday's law states that quantities of various substances, which are liberated or consumed by the action of the electric current, are in all cases proportional to the equivalent weights. This part of the law enables the experimeter to determine with exactness the amount of lead, or lead peroxide, or sulphuric acid which takes part in the reaction when a specified amount of electricity is passed through the cell. The quantity of electricity which liberates one gram-equivalent weight is the same for all substances. It is equal [2] to 96,500 coulombs (see p. 6). This quantity has been named the "faraday" and it is the fundamental constant of electrochemistry. Lead has an atomic weight of 207.20 and a valence of 2, whence the gram-equivalent weight of lead which takes part in the reactions when one faraday of electricity is passed through the solution is $\frac{207.20}{2} = 103.60$ grams.

2. THEORY OF THE LEAD-ACID CELLS

a. Review of the Early Theories.

A number of theories have been proposed to account for the reactions taking place in the lead-acid batteries. The controversies which have arisen over these theories have been acrimonious, but the so-called "double sulphate" theory, which will be described in detail, is now generally accepted. Before this is discussed, a brief résumé of the principal theories which have been proposed will be given.

[2] Vinal and Bates, Sci. Paper of the Bureau of Standards, No. 218.

The first theory, in point of time, is the so-called *oxidation and reduction theory*. This was the original theory of Planté. He believed the lead peroxide to be reduced to lead at the positive plate and the lead of the negative plate to be oxidized during the process of discharge. He recognized the formation of lead sulphate during this reaction, but considered it to be accidental.

According to the *occluded gas theory* the negative plates were supposed to occlude hydrogen, and the positive plates oxygen, during the process of charging. The water was believed to be the real electrolyte, sulphuric acid being added merely to make it conduct. The formation of lead sulphate at the plates was considered a secondary action and an unmitigated evil. This idea has been perpetuated to the present time and forms the basis of much advertising of solutions to eliminate sulphation.

The *double sulphate theory* was first proposed by Gladstone and Tribe in 1882.[3] Their theory met with violent opposition but it has survived to the present day. They discovered that lead sulphate was formed at both plates as part of the process of discharge. They also discovered that the electrolyte became more dilute during the discharge, but Frankland[4] is believed to have been the first to suggest utilizing the change in specific gravity to indicate the state of charge of the battery.

The *persulphuric acid theory* was developed subsequently to the double sulphate theory. It was claimed that persulphuric acid and hydrogen peroxide were formed during the charge and that the electromotive force of the cells depended on these. In 1878 Berthelot had found that persulphuric acid can be formed by electrolysis of sulphuric-acid solutions and that hydrogen peroxide accompanies it. Persulphuric acid is formed when moderately strong sulphuric acid is electrolyzed between platinum electrodes at a high-current density. These are not the conditions which obtain in the storage battery; the specific gravity of the electrolyte is low and the electrodes are more soluble than platinum plates. For these and other reasons it does not seem likely that persulphuric acid in appreciable amounts is formed during the normal operation of storage batteries. Persulphuric acid is known to be destructive to the plates and, if any considerable amount of it were to be formed, the period of useful service of a storage battery would undoubtedly be short.

According to a still more recent theory, which may be termed the *"higher oxide" theory*, the active material of the positive plate is an oxide higher than the peroxide, and on discharge this is reduced to lead peroxide by hydrogen. The reaction at the negative plate during dis-

[3] Nature, January 5, 1882; Electrician, 9, p. 612, 1882.

[4] Proc. Royal Society, 35, p. 67, 1883.

charge is supposed to result in the formation of a lower sulphate, such as Pb_2SO_4, which is spontaneously converted to the ordinary lead sulphate.

Only the double sulphate theory, in support of which there is abundant experimental evidence, has survived to the present time. The discussions in this book are based entirely on the double sulphate theory, which is described in detail.

3. THE DOUBLE SULPHATE THEORY

The double sulphate theory is most conveniently stated by the equation for the reaction

$$PbO_2+Pb+2H_2SO_4 \rightleftarrows 2PbSO_4+2H_2O \quad . \quad . \quad . \quad . \quad (4)$$

From left to right this equation represents discharge, and from right to left, charge. The significance of the term "double sulphate" lies in the fact that lead sulphate is formed at both the positive and negative plates during the process of discharge.

a. Reasons for Believing in its Correctness.

Since the double sulphate theory has met with opposition even in recent times, it is desirable to state the reasons for believing it to be correct.

In the first place, the formation of lead sulphate may be observed at both plates. This fact has been verified by numerous observers since Gladstone and Tribe first discovered it in 1882. Mugdan [5] found, by analysis, 94 per cent of the theoretical lead sulphate at the positive plates and 100 per cent of the theoretical lead sulphate at the negative plates, his calculations being based on the equations for the double sulphate theory in accordance with Faraday's law. His experiments were carried out with an electrolyte containing 26 per cent acid, which is slightly lower in concentration than that customarily used at the present time.

The second piece of evidence for the correctness of the double sulphate theory is found in the measured consumption of the sulphuric acid during the charging or discharging process. Numerous authors have measured the acid consumption, and some of them have obtained results in accordance with the theory. There are, however, serious discrepancies in the results of experimental work. This is not surprising, because of the difficulty in determining the effective amount of electrolyte actually within the cell, and because of the spontaneous oxidation of the negative

[5] Zeit. Electrochem., 6, p. 309, 1899.

plates when exposed to the air. The best-known measurements on this subject confirming the theory are those of Kohlrausch and Heim.[6] Recent experiments to determine the consumption of acid were made by McInness, Adler, and Joubert.[7] Although they found the consumption of acid considerably less than that called for by the double sulphate theory, their experiments on the nature of the active material of the positive plate supported the theory. Their paper shows that, in the preparation of the plates, the negatives were dried in the air, which undoubtedly resulted in the formation of lead oxide in large amount.

In the course of a test of batteries of the aeroplane ignition type, recently made at the Bureau of Standards, it has been found possible to calculate approximately the acid consumption for a discharge of the cells at the normal rate of 2 amperes. This test was made with other objects in view than the determination of acid consumption, and no particular care was bestowed on such parts of the experiment as would affect this determination, but it is interesting to see how close the acid consumption is to the theoretical value even under such circumstances. The results are given in Table XXIX. Two batteries gave calculated values in excess of the actual capacity delivered, while the others gave somewhat lower values. The average algebraic difference of the calculated and observed values is, however, only about 2 per cent.

TABLE XXIX

ACID CONSUMPTION DURING DISCHARGE

Measurements made on four small batteries designed for aeroplane engine ignition. Each battery has four cells. Two batteries of each of two manufacturers.

Battery	Weight Electrolyte, Grams	Electrolyte per Cell, Grams	Initial Specific Gravity, 25° C.	Final Specific Gravity, 25° C.	Initial Volume, cc.	Final Volume, cc.	Initial Equivalent, Ampere-hours	Final Equivalent, Ampere-hours	Calculated Capacity, Ampere-hours	Observed Capacity, Ampere-hours	Difference
A 1	730	182	1.293	1.132	140.0	131.3	19.2	7.7	11.5	10.3	+1.2
A 2	740	185	1.299	1.128	142.5	132.7	20.0	7.5	12.5	11.5	+1.0
B 1	615	154	1.299	1.106	118.6	108.6	16.7	5.1	11.6	11.8	−0.2
B 2	605	151	1.299	1.117	116.6	106.6	16.4	5.5	10.8	11.8	−1.0

There are numerous experimental difficulties to be overcome in making an exact determination of the acid consumption. The principal points are as follows: (1) Accurate determination must be made of the

[6] Elektrotech. Zeit., 10, p. 327, 1889.

[7] Trans. Amer. Electrochem. Soc., 37, pp. 641, 1920.

amount of electrolyte within the cell. If this involves weighing the negative plates dry, they must be washed in distilled water and dried in a vacuum. (2) Equalization of the acid electrolyte must be accomplished in all parts of the plates and cell, including the space between the bridges, if present, before the specific gravity of the electrolyte can be measured. (3) Corrections must be made for the temperature if it is different from some chosen standard, and corrections for the change in volume of the electrolyte during charge and discharge must be made also. (4) Corrections must be made for the amount of sulphate initially present in the plates if this differs from the amount present in the fully charged state. (5) Allowance must be made for two gram-molecules of water formed during discharge for each gram-molecule of lead transformed into lead sulphate.

The third line of evidence for the correctness of the double sulphate theory is that the active materials of the plates correspond to the equation. The active material of the negative plate is sponge lead. The formation of this sponge lead is visible and unquestioned. The active material of the positive plate is lead peroxide, PbO_2. The nature of this positive active material has been called in question, but there are the following lines of evidence to support the statement that it is lead peroxide: (1) It was demonstrated, even before Planté's time, that PbO_2 forms on a lead anode in H_2SO_4, and a recent confirmation of this fact was found by McInness.[8] (2) Streintz,[9] by means of a zinc electrode, showed that the potential difference between zinc and lead peroxide is greater than for any other oxide of lead and is the only one corresponding to the potential of the storage cell. (3) The percentage of PbO_2 in the active mass varies in accordance with Faraday's law, as shown by the work of Ayrton, Lamb, Smith, and Woods.[10] (4) Plates made of chemically prepared lead peroxide behave as ordinary positive plates according to Strecker,[11] but there are two, and perhaps more, allotropic forms of lead peroxide.

The fourth line of evidence for the correctness of the double sulphate theory is indirect, since it is a negation of the alternative theories of occluded gas and the formation of persulphuric acid. Lead occludes little or no hydrogen; oxygen, on the other hand, is known to oxidize the material of the plates on charge to the peroxide state. The occluded gas theory is, therefore, not plausible. Schoop [12] has shown that the

[8] Trans. American Electrochem. Soc., 37, p. 641, 1920.
[9] Wied. Ann., 38, p. 344, 1889.
[10] Jour. Inst. Elect. Eng., 19, p. 539, 1890.
[11] Elektrotech. Zeit., 12, pp. 435, 513, 524, 1891.
[12] Das Sekundär Element, p. 83, 1895.

conditions which favor the formation of persulphuric acid are relatively concentrated solutions and the use of platinum anodes. Such are obviously not the conditions in the storage cell. Lead is attacked by persulphuric acid, and if the latter were present we should hardly expect the long records of satisfactory service that are observed. Mugdan has shown also that persulphuric acid, if present, decreases the voltage of the cell.

The last and most convincing line of evidence for the correctness of the double sulphate theory is the thermodynamic proof. The relation of the heat of the reactions to the available work, the electromotive force, and the temperature coefficient of the voltage, is given by the Gibbs–Helmholtz equation (p. 159). Values for the heat of the reactions have been determined by Streintz [13] and Tscheltzow [14] to be 87,000 and 88,600 calories, respectively. The mean of these values is 87,800 calories, which may be substituted for Q_N in the thermochemical equation of the double sulphate theory.

$$PbO_2+Pb+2H_2SO_4+N\cdot H_2O=2PbSO_4+(N+2)H_2O+Q_N. \quad (5)$$

Q_N is the heat of reaction for a dilution of the acid fixed by N. Their values for Q_N are for dilute acids, and may be corrected by the available values for the heat of dilution (Table X, p. 76) to make them apply to ordinary cells. When this is done, theory and observation correspond, provided the formation of lead sulphate at both plates as a part of the current-producing process is assumed. Experiments by Vinal and Altrup [15] on cells at low temperatures have confirmed the agreement between theory and observation for the temperature coefficient of voltage. Dolezalek [16] has shown that the change in voltage of a cell with some particular change in concentration of the electrolyte agrees with the change in free energy of 2 gram-molecules of electrolyte when changed in density through this range.

By a number of different lines of evidence, adequate confirmation of the double sulphate theory has been furnished.

b. Reactions at the Positive and Negative Plates.

Although the double sulphate theory states that lead sulphate is formed at each plate during the discharge, and gives us an equation for calculating the performance of the cell, it leaves us in the dark about

[13] Wied, Ann., 53, p. 698, 1894.
[14] Comptes Rendus, 100, p. 1458, 1885.
[15] Sci. Paper, Bureau of Standards, No. 434, 1922.
[16] Theory of the Lead Accumulator, p. 62.

the actual processes that go on at the positive and negative plates. It does not tell how the substances are formed, or explain their relation to the transfer of electricity through the cell.

Figure 54 is a diagram which shows in detail the probable processes that result in final products of discharge, according to the double sulphate theory. At the negative plate the process is relatively simple; the solution tension of lead causes it to throw lead ions into solution (see p. 136). These are in the divalent state, carrying two positive charges. Coincident with the departure of each of the positive lead ions from the surface of the electrode surface, the electrode itself acquires two negative charges. The lead ions react with sulphate ions, which have charges of equal magnitude but opposite sign, forming lead sulphate. This is so

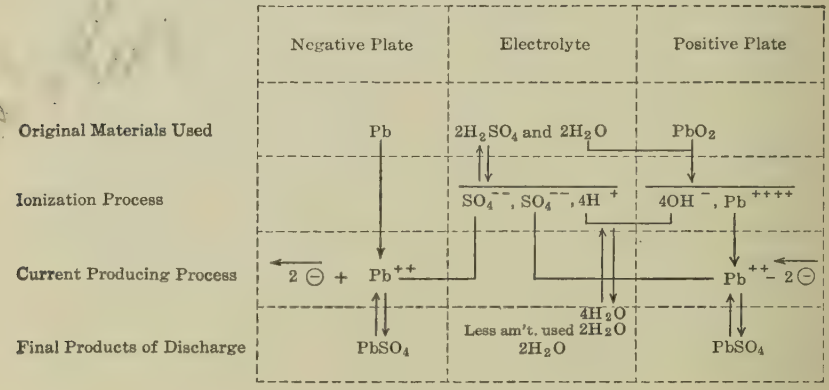

FIG. 54.—Discharge reactions.

nearly insoluble in the electrolyte that it immediately precipitates out of the solution and is deposited on the electrode.

Reactions occurring at the positive plate are not so well understood. They may be explained, however, in several ways. The tetravalent ion theory, which seems the most probable, was proposed by Le Blanc [17] many years ago. Lead peroxide, although insoluble in appreciable amounts in sulphuric acid under ordinary conditions, may pass into solution to a limited extent when the current flows. Small amounts of it, in combination with water, ionize into tetravalent lead ions and monovalent hydroxyl ions, according to the equation:

$$PbO_2 + 2H_2O \rightleftarrows Pb(OH)_4 \rightleftarrows Pb^{++++} + 4OH^- \quad . \quad . \quad . \quad (6)$$

The current-producing process is associated with potential dif-

[17] Lehrbuch der Elektrochemie, 1st ed., p. 223, 1895.

ferences at the electrodes that depend, first, on the equilibrium potentials for the ionic reactions and, second, on the ionic concentrations. At the positive electrode the ionic reaction is

$$Pb^{++++}+2\ominus \rightarrow Pb^{++}$$

and for this the potential difference is about +2.08 volts. Ionization of the electrolyte occurs substantially as follows:

$$H_2SO_4 \rightleftarrows 2H^{+}+SO_4^{--}$$

As a last step in the process of discharge, the combination of lead and sulphate ions takes place, with the formation of lead sulphate which, being practically insoluble in the electrolyte, deposits as a solid substance on the plates. This reaction is represented by Equation (7):

$$Pb^{++}+SO_4^{--} \rightleftarrows PbSO_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

These reactions are shown diagrammatically in Fig. 54. It should be noted that four molecules of water are really formed for each two molecules of sulphuric acid consumed, but as two molecules of water are used up at the same time, the net change is the production of two molecules of water, which is in accordance with the equation for the double sulphate theory (4).

The single potential of the positive plate is given by the formula:

$$E_p=2.08+\frac{RT}{2}\log\frac{[Pb^{++++}]}{[Pb^{++}]}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The concentrations of the ions inclosed in the brackets are small quantities for which no directly measured values are available. R in this equation is the gas constant, and T the absolute temperature.

Similarly, the potential of the negative electrode is obtained. The reaction in this case is

$$Pb-2\ominus \rightarrow Pb^{++}$$

for which the equilibrium potential value (Table XXVIII) is +0.16 and the single potential

$$E_n=0.16+\frac{RT}{2}\log[Pb^{++}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The electromotive force of the cell is the difference between these two single potentials and is given by the expression

$$E=E_p-E_n=2.08-0.16+\frac{RT}{2}\log\frac{[Pb^{++++}]}{[Pb^{++}]^2}. \quad . \quad . \quad (10)$$

Values for R and T are known, and the product RT at ordinary temperatures is $0.0002 \times 290 = 0.058$. The values of the ionic concentrations vary with the concentration of the electrolyte, and it is to be expected, therefore, that the voltage of the cell will vary with the concentration of the electrolyte, as will be shown to be the case in a later section.

The charging process is shown diagrammatically in Fig. 55. Starting with the products of discharge, the lead sulphate at both electrodes passes into solution and ionizes. The water also is ionized as rapidly as equilibrium conditions permit. The divalent lead ions at the negative plate, which is now the cathode, take up two electrons, neutralizing their charges, and then are deposited as lead in the solid state. The divalent

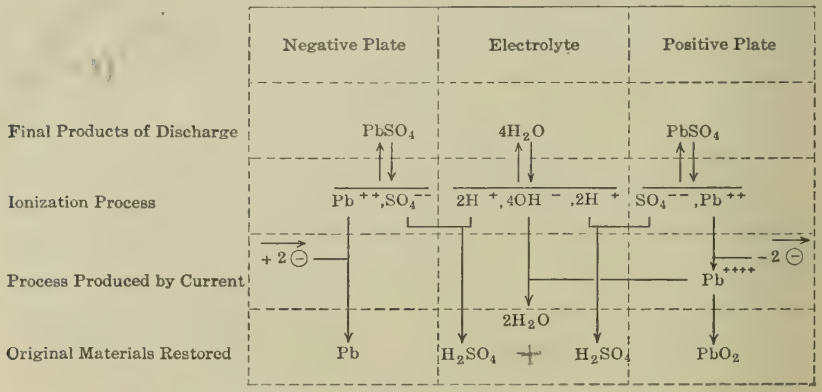

FIG. 55.—Charge reactions.

lead ions at the positive plate or anode are forced by the charging current to give up two electrons, which changes them to the tetravalent state. Each of these ions may then unite with two oxygen ions, through an intermediate step, to form lead peroxide, which is deposited upon the plate. The sulphate ions formed at each plate unite with two hydrogen ions, with an intermediate step, forming sulphuric acid at each plate.

Although the theory given above agrees with the general expression for the double sulphate theory, and although we know from other lines of evidence of the possible existence of tetravalent and divalent lead ions, it cannot be insisted that this is the only or necessarily correct explanation. Several other theories for the reactions at the positive plates are given in the following paragraphs. There appears to be no divergent opinion about the reactions at the negative plate.

The discharge reaction at the positive plate may be regarded as a reduction process in accordance with the ionic equations:

$$PbO_2 + 2\ominus \rightleftarrows Pb^{++} + 2O^{--}$$

$$2H_2SO_4 \rightleftarrows 4H^+ + 2SO_4^{--}$$

$$\left.\begin{aligned} Pb^{++} + SO_4^{--} &\rightleftarrows PbSO_4 \\ 4H^+ + 2O^{--} &\rightleftarrows 2H_2O \end{aligned}\right\} \text{final products}$$

The remaining sulphate ion, SO_4^{--}, which is left over in the above reaction, is required for the process at the negative plate. This theory is not very different from that in Fig. 54, but avoids the assumption of tetravalent lead ions and the solution of lead peroxide as such.

Liebenow [18] has proposed a theory which he bases upon the cathodic production of anions, a process not often observed. He believed the lead peroxide to pass into solution as the anion PbO_2^{--}. This anion then reacts with four hydrogen ions, $4H^+$, forming two molecules of water, and lead ions with two positive charges. The lead ions then reacted with sulphate ions to form lead sulphate, as in the former cases. Liebenow's theory makes it possible to write an equation according to the Nernst theory for the cell voltage, in a form that is simple to study but not easily evaluated.

$$E = \frac{RT}{2} ln \frac{C_p C_n}{[Pb^{++}][PbO_2^{--}]},$$

where C_p and C_n are the solution tensions of the positive and negative active material and the bracketed values represent the corresponding ionic concentrations. It is evident that a decrease in the ionic concentrations would result in an increase in the value of E if other quantities remained the same. On the other hand, the value for E would diminish in alkaline solutions which may contain the anion of lead peroxide, PbO_2^{--}, in appreciable amounts, as the experiments of Liebenow proved, and in solutions containing soluble lead salts. This is found to be the case. A peculiar confirmation of the theory (although involving several assumptions about the applicability of the equation) was found by Vinal and Altrup [19] in experimenting on frozen cells at extremely low temperatures, where extraordinarily large voltages were found. In some cases these exceeded 10 volts per cell, although the current was vanishingly small. The explanation given is as follows:

The freezing of the electrolyte reduces the mobility of the ions practically to zero. If, then, the ions which are in immediate contact with the surface of the electrodes are discharged, they cannot be replaced by the migration of other ions from the electrolyte, and the effect in

[18] Zeit. f. Elektrochem., 2, pp. 420 and 653, 1896.

[19] Sci. Papers of the Bureau of Standards, No. 434, p. 632, 1922.

the region of the electrodes is essentially a decrease in the ionic concentrations. The equation, therefore, suggests the possibility of increased values of E as was observed after the freezing occurred.

In some of the older textbooks there is found an explanation of the chemical reactions at the positive plate that is without reference to the ionic equations. It is assumed that hydrogen is deposited on the cathode, and the reactions resulting are indicated by the following equations:

$$PbO_2 + 2H = PbO + H_2O$$

$$PbO + H_2SO_4 = PbSO_4 + H_2O$$

Lead peroxide is reduced to lead oxide, and this is acted on immediately by the sulphuric acid present, with the formation of lead sulphate. During the process two molecules of water are formed. These equations are all consistent with the double sulphate theory for the reactions occurring during discharge of a storage cell.

4. ENERGY TRANSFORMATIONS

A storage cell of any kind stores electrical energy by virtue of the chemical reactions taking place at the electrodes. Electrical energy is not stored as electrical energy, but as chemical energy. During the charging process the electrical energy is converted into chemical energy, and when the cell is discharged at a later time this chemical energy is reconverted into electrical energy. The law of the conservation of energy governs these transformations. The energy cannot be created from nothing, nor can it be annihilated; therefore, the electrical energy which the cell can supply bears a definite relation to the amount of chemical energy which it contains. We cannot determine the total amount of chemical energy of the cell, but it is possible to determine the change in chemical energy which occurs as the cell is charged or discharged and, by relating this to the electrical measurements, the electrochemical theory of the storage cell may be developed. This theory includes the theory of the chemical reactions and the theory of the energy transformations.

Chemical reactions in general are accompanied by the evolution or absorption of heat of varying amounts, depending on the nature of the reaction. For each reaction the amount of heat energy liberated or absorbed per gram-molecule of the substance is a definite quantity, and is called the "heat of reaction." This may be measured by causing the reaction to occur in a calorimeter, with the provision that the

chemical energy is converted into heat only while the reacting system is maintained at a constant temperature (isothermal process). Such a measurement cannot be made directly on a storage cell, since the charging or discharging of the cell involves electrical energy also.

a. Effect of Concentration of the Electrolyte.

The heat of the reaction in a storage cell includes the reactions at the positive and the negative plates. The value for the heat of reaction in a lead storage cell has been determined by Tscheltzow [20] and Streintz [21] for very dilute solutions of the sulphuric acid (1 molecule of acid to 400 molecules of water). The values which they obtained were as follows:

Tscheltzow	88,600 calories
Streintz	87,000 calories
Mean	87,800 calories

The thermochemical equation of the lead storage cell with this dilute electrolyte may be written

$$PbO_2 + Pb + 2H_2SO_4 + n \cdot H_2O \rightleftarrows 2PbSO_4 + (n+2)H_2O + 87{,}800 \text{ calories},$$

where $n = 800$ molecules of water.

To apply this to a practical case it is necessary to add to the heat of reaction a correction which depends on the heat of dilution of the sulphuric acid (p. 76) for any required concentration above that of the dilute electrolyte ($2H_2SO_4 \cdot 800\ H_2O$). The reason for adding this correction may be made apparent in several ways. The heat evolved during the dilution of the sulphuric acid depends on the amount of the dilution and is a measure of the change in its intrinsic energy. A relatively concentrated solution has liberated less energy in the form of heat per gram-molecule than a dilute solution, and therefore possesses greater intrinsic energy. For dilute solutions as compared with those more concentrated, the energy will be less by the quantity of heat evolved by dilution of the acid, since the chemical action must take the acid from the dilute liquid.

b. Relation of the Energy Changes to the Maximum Work Obtainable.

The heat of the reaction, which has been designated in the preceding sections as Q, represents the change in the total energy of the cell during a reaction that is purely chemical. The next step is to consider the

[20] Comptes Rendus, 100, p. 1458, 1885.
[21] Wied. Ann., 53, p. 698, 1894.

cell as an electrochemical apparatus in which the chemical energy becomes electrical energy. If all of the chemical energy could be converted into electrical energy, and vice versa, we should have an ideal cell from the theoretical standpoint. There would be no heat evolved or absorbed, and the chemical and electrical energy would be so simply related that the voltage of the cell might be calculated at once, as proposed by Lord Kelvin and von Helmholtz many years ago. This is unfortunately not the case, as they both subsequently recognized.

Thermochemical Equations.—The heat of the reaction in the cell depends on the heats of formation of the various substances taking part in the reaction. The heat of formation may be defined as the number of calories liberated or absorbed during the formation of one gram-molecular weight of the compound. For example, the heat of formation of lead oxide is 50,300 calories and is expressed by the formula:

$$Pb+O \rightarrow PbO+50{,}300 \text{ calories}$$

The heat of the reaction expresses the difference between the energy content of the reacting substances and that of the product formed. If this difference is positive, heat is liberated and the reaction is said to be "exothermic"; but if it is negative, heat is absorbed and the action is "endothermic." Conversely, the decomposition of exothermic compounds is accompanied by the absorption of heat and this fact may be designated in the equations by a minus sign. Decomposition of endothermic compounds is accompanied by the evolution of heat. The heats of formation of many substances are known, and from the available data the thermochemical equation of the storage cell may be written. The heats of formation are written beneath the symbols; decomposing substances are on the left and substances formed on the right.

$$PbO_2+2H_2SO_4+Pb \rightarrow 2PbSO_4+2H_2O$$
$$-62{,}400-385{,}840 \qquad +432{,}420+136{,}828$$

Lead, being an element, has no heat of formation. The balance is 121,008 calories in favor of the right-hand side of the equation. The above does not represent strictly the ordinary reaction, because no account has been taken of the fact that the sulphuric acid in the cell is diluted with water and not concentrated as represented by the formula. The heat of dilution of the acid has been given on page 76. Revising the above formula for acid of specific gravity 1.288 at 15° C.,

$$PbO_2+2H_2SO_4\cdot 18H_2O+Pb \rightarrow 2PbSO_4+2H_2O$$
$$-62{,}400-(385{,}840+29{,}900) \quad +432{,}420+136{,}828$$

The balance in this case is 91,108 calories in favor of the right-hand side of the equation. This amount is nearly the same as that obtained by Streintz and Tscheltzow (see p. 155) if their values are corrected for the heat of dilution of the acid.

The thermochemical equation shows that more than 90,000 calories is involved in the discharge. If only heat energy were involved, this would mean that the cell would become very hot, but this is obviously not the case. The cell may even cool during the discharge. These apparently contradictory facts are reconciled by the fact that the 90,000 calories represent heat energy which is transformed into electrical energy during the discharge. It does not appear as heat. By Kelvin's rule, if the heat of the chemical reaction is transformed into useful work (electrical) by processes that are completely controllable and exactly equivalent, then we may calculate the voltage of the cell from the equation:

$$E = \frac{4.183Q}{96{,}500 \times 2}$$

One calorie equals 4.183 volt-coulombs. The volt-coulomb is an electrical unit of energy equal to one ampere flowing under a pressure of one volt for a period of one second. It might be called the joule or the watt-second, but the term volt-coulomb is particularly appropriate for electrochemical usage because the coulomb is the fundamental unit in determining the extent of electrochemical reactions and this multiplied by the electrical pressure expresses the energy. The factor 96,500 is the number of coulombs required for the transformation of one gram-equivalent of the active material of the plates, which for the lead battery has a valence of 2. It is evident, therefore, that the voltage E expressed in volts may be calculated from the number of calories liberated during the reaction. By this formula the voltage for the cell in concentrated acid, for which Q was found to be 121,008 calories, is calculated to be 2.62 volts. This value agrees very well with the value found experimentally by Gladstone and Hibbert, which was 2.607 volts. The ordinary cell in dilute sulphuric acid (specific gravity 1.288) for which Q equals 91,108, is calculated to have a voltage of 1.975 volts, but by experiment the value is found to be about 2.12 volts. Wade[22] has pointed out the necessity for making a correction to the calculated value to allow for the water which was combined with the sulphuric acid consumed during the reaction, because this and the two gram-molecules of water formed, dilute the main body of the electrolyte, liberating a small amount of energy. In the ordinary cell, the electrolyte having a

[22] Secondary Batteries, p. 243.

specific gravity 1.288, 5820 calories are liberated for every equivalent of the active materials transformed. This corresponds to 0.126 volt which, added to the value computed above, gives 2.10 volts as the final value.

The agreement between the values calculated by Kelvin's rule and the values determined experimentally is closer in the case of the lead storage battery than for most other types of batteries. Both Lord Kelvin and von Helmholtz recognized in later years that the relation of the heat of the reaction to the electromotive force is not strictly in accord with the above equation. This is because there is, in addition to the heat of the reaction, another and uncontrollable heat effect which cannot be neglected. The nature and magnitude of this additional quantity of energy will now be discussed.

Reversible and Irreversible Heat Effects.—If a storage cell of the lead-acid type be placed in a calorimeter which will permit the making of accurate measurements of heat evolved or absorbed during charge or discharge, it will be found that the cell absorbs a small amount of heat from its surroundings during discharge and gives out a similar amount during charge. This means that on discharge the cell delivers more useful work than is represented by the heat of the chemical reactions taking place in it, but that correspondingly more energy is required to charge it. Stated in another way, it means that the cell on discharge draws heat energy from its surroundings and converts it into useful work. Several names have been proposed for the heat liberated or absorbed during the charge or discharge of the cell, but none of them have come into common use. One of these is "reversible heat," which distinguishes this heat from the irreversible heat which is generated in the cell during its operation owing to the ohmic resistance. The latter is proportional to the square of the current. The reversible heat effect is directly proportional to the current, because it is dependent on the extent of the electrochemical action. Another name which has been proposed is the "latent heat" of the cell, suggested by the analogy of the heat energy liberated or absorbed when water freezes or ice melts. A third proposal has been to call it the "Helmholtz heat," to distinguish it from that due to the I^2R loss within the cell, for which the name "Joule heat" has been sometimes used. This reversible heat effect will be designated by q.

The maximum useful work which the cell can deliver is the quantity of electricity (current$\times$time) expressed in coulombs, multiplied by the electromotive force. This is sometimes called the free or available energy, to distinguish it from the total energy as represented by the heat of the reaction. The available energy will be designated by W.

By the first law of thermodynamics, the change in the total energy of cell Q, considered as a system, is equal to the sum of the external work W, done by the system, and the heat evolved, q. This is expressed by the equation:

$$Q = W + q$$

The heat of the reaction, Q, is measured in calories. The calorie is also called the gram-calorie. This unit of heat energy may be converted into its electrical equivalent of energy, by the following relation: 1 calorie (20° C.) = 4.183 volt-coulombs.

The available energy of the cell, W, is naturally expressed in volt-coulombs. The latent heat of the cell is measured in calories.

We may now apply the equation $Q = W + q$ directly to the case of a lead-acid storage cell, using the following experimental data:

Open-circuit voltage	2.120
Specific gravity of electrolyte at 25°	1.280
Heat of reaction (see p. 155)	87,800
Correction for heat of dilution (see p. 76)	4,420
Coulombs per gram-equivalent	96,500
Valence	2

$$q = (87{,}800 + 4420) - \frac{2.120 \times 96{,}500 \times 2}{4.183} = -5595 \text{ calories}$$

The value for q is negative and represents about 6 per cent of the total energy delivered by the cell. The significance of the minus sign is that the cell has a tendency to cool on discharge, or must absorb heat from the surroundings if its temperature is kept constant.

5. VOLTAGE

a. Relation of Voltage to Temperature.

The Gibbs-Helmholtz Equation.—In the preceding section it was found that the total change in energy during discharge is equal to the sum of electrical energy delivered and a small quantity of energy in the form of heat, which, for lack of a better name, is called the latent heat of the cell. The equation expressing this relation is

$$Q = W + q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The quantity q may be either positive or negative, but for the lead-acid storage cell it is negative.

It is a well-known fact that the voltage of any kind of voltaic cell varies more or less with the temperature. The change in voltage per

degree change in temperature for a lead-acid storage cell is so small that for practical purposes it may be neglected, but it is of importance from a theoretical point of view. Before attempting to determine the actual magnitude of the temperature coefficient, we shall derive,[23] from theoretical considerations, the celebrated Gibbs-Helmholtz equation, which shows the relation of the energy transformations, voltage, and temperature. It will then be possible to make comparisons of the observed quantities with those calculated from thermodynamic reasoning.

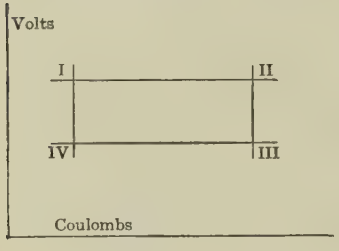

FIG. 56.—Cyclic process.

Let it be assumed that a storage cell of the lead-acid type has an open-circuit voltage of E when the absolute temperature is T, and that the cell is in equilibrium with its surroundings. It is also assumed that a quantity of electricity, designated by e, may be passed through the cell either as a charge or discharge, and that the cell may be kept at a uniform temperature (isothermal process) or completely insulated to prevent the transfer of heat (adiabatic process) as we may desire.

The following cyclic process is to be carried out:

I. Let the initial state of the cell be described by the open-circuit voltage E and the temperature T, at the point marked I on the diagram (Fig. 56). Then let a quantity of electricity, e, pass through the cell in the discharging direction while the temperature is held constant at T by furnishing a small amount of heat as required by the term q in the equation above. The current must be small during this process, so that irreversible heat effects due to the ohmic resistance of the cell may be neglected. The work, in volt-coulombs, done by the cell during this part of the cycle is $W_1 = Ee$.

II. When the quantity of electricity, e, has passed through the cell, let the isothermal process be changed momentarily to adiabatic, during which time the temperature of the cell will fall by an infinitesimal amount δT, becoming $T - \delta T$. The open-circuit voltage becomes $E - \left(\frac{\partial E}{\partial T}\right)\delta T$,

[23] Theory of Thermodynamics, by Buckingham, p. 140.

where $\left(\frac{\partial E}{\partial T}\right)$ is the temperature coefficient when no current is flowing.

III. Let the quantity of electricity, e, pass through the cell in the charging direction while the temperature is held at $T-\delta T$. The amount of work done on the cell during this process is $W_3=\left[E-\left(\frac{\partial E}{\partial T}\right)\delta T\right]e$.

IV. When the quantity of electricity, e, has passed through the cell, let the isothermal process be changed to adiabatic while the temperature of the cell increases by the amount δT, which restores the cell to its original temperature. The total external work done by the cell during the cycle is

$$W_1-W_3=Ee-\left[E-\left(\frac{\partial E}{\partial T}\right)\delta T\right]e=e\left(\frac{\partial E}{\partial T}\right)\delta T=\delta q$$

The adiabatic processes are infinitesimal in length and are negligible.

Considering, for a moment, the cell as a purely chemical apparatus, we shall suppose chemical reactions to take place in amount and direction equivalent to the discharge of one coulomb. The heat of this reaction is to be measured in volt-coulombs and designated by Q'. For a discharge equivalent to e coulombs, the heat of the reaction will be $Q'e$. The electrical energy of the corresponding reactions at temperature T is equal to Ee. The difference in these two quantities gives at once the amount of heat supplied by the constant temperature reservoir at temperature T during the first step of the cyclic process. This is the latent heat of the cell q. It is equal to the difference between the electrical energy and the heat of the reaction:

$$q=Ee-Q'e$$

According to Carnot's cycle, the ratio of the amount of heat converted into useful energy (which in this case is electrical) to the amount of heat received by the system when held at the upper temperature during the cyclic process, is related to the absolute temperature according to the equation

$$\frac{\delta q}{q}=\frac{\delta T}{T}$$

Substitution of the values for δq and q may now be made in this equation

$$\frac{e\left(\frac{\partial E}{\partial T}\right)\delta T}{Ee-Q'e}=\frac{\delta T}{T}$$

or

$$T\left(\frac{\partial E}{\partial T}\right)=E-Q'$$

the relation of Q' to Q when measured in calories is

$$\frac{96{,}500Q'}{4.183}=Q$$

and the final equation becomes

$$\frac{Q}{23{,}070}=E-T\left(\frac{\partial E}{\partial T}\right). \quad . \quad . \quad . \quad . \quad (12)$$

This is the celebrated Gibbs-Helmholtz equation applied to a reversible electric cell. The equation shows, first, that the value of the voltage depends on the concentration of the electrolyte since it was shown on page 157 that Q varies with the concentration. It also shows that the term q in Equation (11) is the product of the absolute temperature and the temperature coefficient of the voltage, and that this coefficient also varies with the concentration of the electrolyte. For any given temperature and concentration of the electrolyte, the temperature coefficient may at once be calculated if the voltage of the cell is known. In the next section the observed and calculated values of this coefficient will be compared.

The Temperature Coefficient.—By the temperature coefficient is meant the change in open-circuit voltage with change in temperature; it should not be confused with the change in capacity that is caused by changes in temperature. The agreement between the measured and calculated values of the coefficient affords one of the best confirmations of the correctness of the double sulphate theory.

The coefficient is most conveniently expressed as the change in voltage per degree change in temperature. The coefficient is positive within the working range, that is, a rise in temperature is accompanied by a rise in voltage. The coefficient is constant, which means that the same values for the change in voltage are found for a degree change in temperature, irrespective of the actual temperature of the cell.

An experimental determination of the temperature coefficient has been made by Vinal and Altrup [24] within the range $+25°$ to $-72°$ C.

[24] Sci. Papers of Bureau of Standards, No. 434, 1922.

By going to low temperatures, the effects of local action, which increase rapidly at high temperature, were avoided, and at the same time a wide range of temperatures was obtained. The storage cell which was used was contained in a test-tube and was surrounded by ground cork in a double-walled jacket similar to a Dewar vessel, but having air at atmospheric pressure between the walls. The double-walled glass vessel was then placed in a bath of gasoline cooled by carbon-dioxide snow. By this means the cooling was made gradual, about two hours being required for the temperature of the cell to fall from the initial to the final value. During this time readings of the voltage were taken on a potentiometer. The temperatures were measured by a calibrated thermo-couple. The voltage readings are given in the following table as they are of practical importance because automobile batteries and aeroplane batteries are exposed to low temperatures in cold climates and at high altitudes.

TABLE XXX

Open-circuit Voltages of Storage Cells

(Variation of voltage with temperature of fully charged cell containing electrolyte of 1.280 specific gravity at 25° C.)

Temperature		Voltage
° C.	° F.	
20	68	2.116
10	50	2.113
0	32	2.111
−10	14	2.107
−20	− 4	2.103
−30	−22	2.100
−40	−40	2.096
−50	−58	2.092
−60	−76	2.087
−70	−94	2.081

As freezing did not occur in this range, an accurate estimate of the temperature coefficient may be made, since the cell had sufficient time for thermal equilibrium to be established at the beginning and end of the experiment. The temperature coefficient was found to be

0.000398 volt per degree C.

or

0.000221 volt per degree F.

It is interesting to compare this result with the value computed from the Gibbs-Helmholtz equation and the available thermochemical data. Equation (12) on page 162 becomes:

$$\frac{dE}{dT}=\frac{1}{T}(E-0.000021674Q)$$

Substituting for E, the initial value for the cell at 25° C.; and for T, the absolute temperature of the cell, 298°, at the beginning of the experiment; and for Q the heat of the reaction corrected to the specific gravity 1.280 (p. 76), we obtain as the calculated value for the temperature coefficient, $\frac{dE}{dT}=0.000407$ volt per degree C.

The agreement of the observed and calculated values is better than would be expected, and gives a striking proof of the validity of the Gibbs-Helmholtz equation over a wide range of temperature. It should be noted also that the thermochemical data are based on the equation for the double sulphate theory (see p. 146).

Referring to Equation (12) it is seen that both E and Q are dependent on the concentration of the electrolyte and therefore the temperature coefficient is also dependent on the concentration. Since Q decreases as the concentration diminishes and E does also, as will be shown in the next section, the temperature coefficient varies as the difference of two diminishing quantities as the concentration decreases. We cannot tell therefore, from the equation, whether the coefficient will increase or decrease. Dolezalek [25] has made measurements of the temperature coefficient over a wide range of concentrations. His value for acid of specific gravity 1.280 is somewhat less than that given above. At 1.120 sp. gr. his measured value is about 0.00038 volt per degree C. This measured value, together with the coefficient at 1.280 sp. gr., obtained by Vinal and Altrup, makes it seem probable that, throughout the range of concentrations ordinarily used for storage batteries, the coefficient may be assumed to be within 0.00038 to 0.00040 volt per degree C., or 0.00021 to 0.00022 volt per degree F. Below the specific gravity 1.120 the coefficient decreases rapidly, according to Dolezalek, passing through zero at 1.040 sp. gr. and becoming negative for all concentrations smaller than this.

Careful determinations of the temperature coefficient have also been made by Thibaut.[26] His values are somewhat less than those given above and less than the theoretical values. Within the range of specific gravities from 1.100 to 1.300, his values all lie between 0.0002 and 0.0003

[25] Theory of the Lead Accumulator, p. 96.

[26] Ref. on p. 166.

volt per degree. He has confirmed Dolezalek's observation that the temperature coefficient passes through zero in the region of 1.040 sp. gr.

All of the determinations mentioned above were made directly on the voltage changes accompanying a change in temperature. There is another, but indirect, method that can be used, since it was shown on page 162 that the reversible heat absorbed during discharge and liberated during charge is equal to the temperature coefficient multiplied by the absolute temperature.

$$q = T\frac{dE}{dT}$$

Streintz [27] has made such a measurement, using an ice calorimeter to determine the heat liberated. He could separate the reversible from the irreversible heat effects, since the former is positive on charge and negative on discharge, while the latter is positive in both cases. The latter depends on the square of the current and the resistance. Streintz therefore obtained the following equations from which to calculate the value of q.

Total heat effect, discharge $h = I^2R - qI$,

Total heat effect, charge $h' = I^2R + qI$;

whence,

$$q = \frac{1}{2I}(h' - h)$$

By making I the same on charge and discharge and keeping it a small quantity, so that there would be a negligible difference in the resistance of the cell, he obtained two values of the coefficient at the specific gravity 1.155, which were 0.000345 and 0.000326. These agree very well with the directly measured values. Other values did not agree so well.

b. Variation of the Voltage with the Acid Concentration.

The open-circuit voltage of the lead storage cell varies with the concentration of the acid which it contains. Measurements of the relation between voltage and concentration have been made by many observers. It has been difficult to compare their results because of the various means that they have used to express the concentration. Some have used specific gravities, others have employed percentages, gram-equivalents, the Baumé scale, etc. In the following table are summarized voltages of the various observers calculated to a uniform scale of specific gravities. The decrease in voltage of the cell on discharge is

[27] Wied. Ann., 49, p. 565, 1893.

attributed largely to the decrease in concentration of the acid in the pores of the plate, and similarly the rise in voltage during charge is attributable in part to the increase in concentration of the acid within the pores. The open-circuit values are of use in fixing the conditions for floating batteries.

TABLE XXXI

VARIATION OF VOLTAGE WITH THE ACID CONCENTRATION

Specific Gravity	Preece, 1883	Heim, 1889	Streintz, 1892	Gladstone and Hibbert, 1892	Dolezalek, 1904	Jumau, 1907	Thibaut, 1913	Vinal and Altrup, 1922
1.010	...	...	....	1.788	....	....	....	....
1.020	...	...	....	1.851	....	....	....	....
1.030	...	...	....	1.880	....	....	....	....
1.040	...	...	....	1.898	....	1.873	....	1.890
1.050	...	...	....	1.913	1.906	1.882	1.877	1.903
1.100	1.934	2.002	1.935	1.963	1.965	1.925	1.934	1.956
1.150	1.939	2.042	1.971	2.003	2.010	1.965	1.987	2.000
1.200	2.040	2.087	2.006	2.038	2.051	2.003	2.040	2.045
1.250	...	2.134	2.040	2.069	2.094	2.042	2.092	2.091
1.300	...	...	2.070	2.099	2.142	2.080	2.140	2.138
1.350	...	...	2.101	2.127	2.188	2.118	....	....
1.400	...	...	2.136	2.154	2.233	2.157	....	....

References for table:

Preece, Proc. Roy. Soc., 35, p. 252, 1883.
Heim, Elektrotech. Zeit., 10, p. 88, 1889.
Streintz, Wied. Ann., 46, p. 454, 1892.
Gladstone and Hibbert, J. Inst. Elec. Eng., 21, p. 425, 1892.
Dolezalek, Theory of the Lead Accumulator, p. 55, 1904.
Jumau, Les Accumulateurs Electrique, p. 126, 1907.
Thibaut, Zeit. Elektrochem., 19, p. 881, 1913.

It is possible to show, from theoretical considerations, why the voltage must increase when the concentration of the electrolyte is increased. The product of the concentrations of the hydrogen and hydroxyl ions is equal to a constant, K,

$$[H^+][OH^-] = K$$

If the percentage of sulphuric acid in the electrolyte is changed, an increase in the specific gravity means an increase in the concentration of the hydrogen ions and a corresponding decrease of hydroxyl ions. Applying this to Equation (6) on page 150, an increase in acidity causes

the reaction to proceed to the right, and equilibrium conditions require an increase in the concentration of the tetravalent lead ions in proportion as the hydroxyl ions decrease. Equation (8) for the potential of the positive plate shows that the potential increases as the concentration of the tetravalent lead ions increases. Coincident with the increase in concentration of the hydrogen ions there is an increase in concentration of the sulphate ions. Equilibrium conditions for Equation (7) on page 151 show that this condition must be accompanied by a decrease in the concentration of the divalent lead ions. This also results in increasing the potential of the positive plate, as Equation (8) shows. Turning now to the potential of the negative plate, by Equation (9) it is apparent that a decrease in the concentration of divalent lead ions, accompanying an increase in concentration of the electrolyte, results in a smaller value for the potential of the negative plate; but as this is to be subtracted from the potential of the positive plate to obtain the voltage of the cell, the effect is in the same direction as for the positive plates. Experiments by Dolezalek [28] have shown that for an increase in acid strength from 6 to 16 per cent, the increase in potential of the positive plates is 0.06 volt and the decrease in potential of the negative plates for the same change in concentration is only 0.004 volt. The change in voltage of the cell is, therefore, the sum of these values, or 0.064 volt. It is at once apparent that the positive plates are much more sensitive to the changes in concentration of acid than the negatives. Considering the cell as a whole, as in Equation (10), it is found that the voltage increases as the concentration of the tetravalent lead ions increases and as the square of the concentration of the divalent lead ions decreases. The observed facts are in agreement with the theory, but reliable data are lacking as to the magnitude of the concentrations of the ions upon which a computation of the quantitative effects can be based.

6. THEORY OF THE NICKEL-IRON CELLS

It is generally agreed that the reactions taking place in the nickel-iron cells consist of the transfer of oxygen from one plate to another. When the cells discharge, oxygen is taken from the nickel or positive plate and added to the iron or negative plate. During charge the reverse action takes place. The electrolyte as a whole does not change in composition or density; but there are, nevertheless, important changes in the electrolyte within the pores of the plates. The changes at the negative plate counterbalance the changes at the positive plate, as will be shown later, and therefore the electrolyte does not appear to change.

[28] Theory of the Lead Accumulator, p. 80.

a. Equations for the Reaction.

Although the general character of the reactions is known, the exact nature of the reacting substances and the chemical formulas for them are in some doubt. The process is not as well understood as in the case of the lead-acid cells. It is interesting to compare the various equations for the reactions that have been proposed. Some of them obviously are incorrect. It is hardly possible to state with certainty that any one of them is the correct one, but some of them seem more probable than the others.

Junger, in a Swedish patent dated January 29, 1901, gave the following as the equation:

$$NiO_2+2Fe(OH)_2+H_2O \rightleftarrows NiO+2Fe(OH)_3$$

This and the succeeding equations are to be read from left to right for discharge, and from right to left for charge. The work of Foerster [29] has indicated that nickel peroxide, NiO_2, is the primary oxidation product at the positive plate as a result of charge, but that it is not stable and passes over to the sesquioxide, Ni_2O_3, with the evolution of oxygen. The symbol NiO_2 could, therefore, represent the active material of the positive plate only at the time of completing the charge. The active material of the negative plate is given as a hydrate of the iron.

Roeber [30] proposed the formula

$$NiO_2+Fe \rightleftarrows NiO+FeO$$

which is delightfully simple. On the basis of this formula he developed an important theoretical discussion of the changes which occur in the electrolyte at the two electrodes during charge and discharge. Although his equation probably is not correct, the interest and value of his theoretical discussion is not diminished and it will be referred to further on.

Another equation found in the literature [31] is the following:

$$2NiO_2+2KOH+Fe \rightleftarrows Ni_2O_3+2KOH+FeO$$

This equation probably represents what happens when the cell is standing idle at the conclusion of a charge, more nearly than it represents the ordinary discharge process, since the NiO_2 spontaneously changes into Ni_2O_3 and the iron also oxidizes slowly to an oxide or a hydroxide.

[29] Elektrochemie Wässeriger Lösungen, 3rd ed., p. 270, 1922.
[30] Electrical World, 37, p. 1105, 1901.
[31] Pender, Handbook for Electrical Engineers, p. 77, 1917.

The discharged state of the nickel electrode is quite certainly lower than the sesquioxide, Ni_2O_3.

Kammerhoff [32] and others have given the equation for the Edison cell as follows:

$$2Ni(OH)_3+Fe \rightleftarrows 2Ni(OH)_2+Fe(OH)_2$$

It is probable that both the iron and nickel oxides in the alkaline solution are hydrated, and this equation is referred to by Allmand as the usual equation. Foerster, in referring to this equation, states that the nickel-iron cell is not independent, theoretically, of the electrolyte. Practically, however, the cell is independent of the electrolyte and this equation has much to recommend it.

Two other equations remain to be mentioned, as they are frequently seen in the literature. The first of these is

$$6NiO_2+3Fe \rightleftarrows 2Ni_3O_4+Fe_3O_4$$

which is given in the National Educational Association monograph. This equation is subject to the objection that nickel peroxide is not a stable compound, and Ni_3O_4 may be considered as a combination of Ni_2O_3 and NiO. The fully discharged plate may have a lower percentage of oxygen than is represented by this formula.

Allmand [33] gives the equation in its simplest form as

$$Ni_2O_3+Fe \rightleftarrows 2NiO+FeO$$

This equation is perhaps the most convenient one to use, and it shows very clearly the transfer of oxygen from one plate to the other during charge and discharge. This equation is implied, but not given explicitly, by the Edison Storage Battery Company in certain of its publications.

b. Reactions at the Plates.

Just as in the case of the lead battery, the general equation for the reaction does not tell the whole story of the reactions at the separate plates. The charging process produces an oxidation of the materials in the positive plate, but these are not homogeneous. It has been supposed that the various oxides of nickel form a solid solution. The lowest oxide, NiO, and the highest, NiO_2, may react to give the sesquioxide, Ni_2O_3; and Ni_3O_4, which is next to the lowest oxide, is considered

[32] Der Edisonakkumulator, p. 13, 1910.

[33] Applied Electrochemistry, p. 239.

a combination of NiO and Ni_2O_3. During charging, the lowest oxide, NiO, takes up the oxygen liberated by the charging current, and later, as the percentage of NiO which is present decreases, there is some further oxidation of the Ni_2O_3 also. The freshly charged plate contains more oxygen than corresponds to the formula Ni_2O_3. The peroxide, NiO_2, is considered the final product, but because of its instability the proportion of oxygen in the fully charged plate does not equal that indicated by the formula. Foerster has stated that the potential of the fully charged plate is determined by the peroxide, however. Since the potential of the peroxide is higher than that of the stable compound, the sesquioxide, into which it decomposes, the voltage of a freshly charged cell falls, soon after the charge is discontinued, by about 0.13 volt, to an equilibrium value of about 1.35 volts, open-circuit value.

This spontaneous reaction has certain interesting consequences, as shown by a study of the performance of cells of the nickel-iron type. The decomposition of NiO_2 to Ni_2O_3 is accompanied by the liberation of oxygen, which causes the popping of the caps for a considerable time after charging has ceased. The discharge of the cell soon after the completion of the charge will show a slightly greater average voltage and capacity than a similar discharge after one or more days. This is an important point to recognize in testing nickel-iron batteries, since differences in procedure will produce variations in voltage, watt efficiencies and capacities. There is abundant experimental evidence to show that little gas escapes from the cells if they are put on discharge soon after the termination of the charge, as compared with the amount of gas which escapes if the cells stand idle. This indicates that the oxygen which escapes spontaneously can be made use of. It also explains why the "noon hour boost" for vehicle cells in heavy service is so effective in making them "lively," aside from the mere number of ampere-hours that are added to their capacity. Lastly an explanation is offered for the well-known fact that the rate of loss of capacity of the nickel-iron cell is considerably more during the first two days after charging than subsequently. It is often stated that a partially discharged nickel-iron battery will lose less charge proportionately, when standing idle, than one fully charged. This rather peculiar fact is explained by the instability of the nickel peroxide.

In passing from the fully charged to the discharged condition, the oxygen content of the materials decreases from an amount somewhat greater than that indicated by the formula Ni_2O_3 to an amount equivalent to Ni_3O_4 or less. The amount of oxygen subtracted from the nickel plate is added to the iron plate.

Roeber [34] has developed an interesting theory of the process, based on his assumed equation for the cell reaction:

$$NiO_2+Fe \rightleftarrows NiO+FeO$$

While this equation may not exactly represent the facts, it does not materially lessen the value of his theory as a basis for affording a picture of the general processes that occur.

The electrolyte, potassium hydroxide, is dissociated into K^+ ions and OH^- ions. Both of these are monovalent and one gram-ion is therefore equivalent to 96,500 coulombs. During discharge K^+ ions are set free at the nickel electrode. Each K^+ ion takes from the electrode one electron, and the potassium atom immediately reacts with water and one oxygen atom taken from the nickel peroxide, to form potassium hydroxide. After 96,500 coulombs have passed through the cell, the reaction may be represented by the equation:

$$NiO_2+2K^++H_2O \rightarrow NiO+2KOH-2\ominus$$

but we may just as easily write the equation for the reaction starting with Ni_2O_3 as the active material. This equation shows that the solution becomes more concentrated at the positive plate during discharge, the opposite of what happens in the lead cell.

At the negative plate the discharge of OH^- ions occurs, oxygen is given up to the iron, and water is formed. The equation may be written:

$$Fe+2OH^- \rightarrow FeO+H_2O+2\ominus$$

Comparing this equation with that given above, it is seen that the water consumed at the positive plate is restored by the action at the negative, and the two molecules of potassium hydroxide formed at the positive plate just balance the two that disappear. The net result is, therefore, the reduction of the nickel oxide and the oxidation of the iron by equivalent amounts. The electrolyte does not appear to change.

Unfortunately, the reactions that actually take place are not quite as simple as those given above. Both the oxides of nickel and iron in the alkaline solutions are somewhat hydrated, and, as Foester has shown, there is a slight tendency for the electrolyte to become more concentrated. The amount of this change is entirely negligible for practical purposes. The reaction at the negative plate will not proceed indefinitely. Passivity effects eventually cause an oxidation of the hydroxide formed by the first reaction, which may cause an extension of the discharge curve

[34] Electrical World, 37, p. 1105, 1901.

of the negative plate at a voltage lower than that ordinarily observed. The discharge of the nickel-iron cell is limited by the positive plate, and therefore this region of the second reaction of the negative plate is seldom reached and is of little practical importance.

The restoration of the active materials to the charged state is brought about by the passage of an electric current through the cell in the opposite direction to that of the discharge, as in the case of the lead-acid batteries. Hydroxyl ions, OH^-, now are liberated at the nickel plate, and potassium ions at the negative plate. The charging reactions may be written as follows:

Positive plate $\quad NiO+2OH^- \rightarrow NiO_2+H_2O+2\ominus$

Negative plate $\quad FeO+2K^++H_2O \rightarrow Fe+2KOH-2\ominus$

During charge, the solution becomes more dilute at the nickel plate and more concentrated at the other, but the two effects balance and the electrolyte as a whole appears to remain constant in composition.

Certain irreversible effects, resulting in the liberation of gas during the charging period, occur in the nickel-iron batteries as in the lead storage battery. Gassing of the negative plate begins soon after charging commences. Hydrogen is liberated and plays a most important rôle in the operation of the battery, since it makes the iron active in spite of its tendency to become passive in an alkaline solution. A liberal proportion of the hydrogen is probably absorbed by the iron. The necessity for the liberation of hydrogen at the negative plate is the explanation of the saying, familiar among battery service men, that if the battery does not gas it is not taking the charge. The rate of liberation of the gas is dependent on the amount of the current flowing, and therefore the rate of charging can affect the subsequent output of the battery. Low-rate charging of nickel-iron batteries is not advisable. During the latter part of the charging period, oxygen is also liberated. The oxygen and hydrogen are given off in about equal amounts for the middle portion of the charge, changing slowly to two parts of hydrogen to one of oxygen as the end of the charge is reached. This means, of course, that at the end the charging current is merely electrolyzing the water present in the cell.

Schoop [35] has made an interesting series of experiments on this type of cell, with electrodes suspended from the arm of a balance so that changes in weight could be measured as the cells discharged. He found changes in the volume of the active material to occur during

[35] Electrochem. Ind., 2, pp. 272 and 310, 1904.

charge and discharge. His experiments show that the active material of the positive plates decreased in volume during discharge and increased during charge. The change in volume is considerable and therefore the tubes of the positive plates in the Edison cell are made very strong and reinforced by steel rings. Changes in volume at the negative plate are smaller and of less importance. Schoop states that the volume decreases at this plate also during discharge. It is rather hard to reconcile this fact with the supposed transformation of iron to iron oxide, but the explanation may lie in the hydrated condition of the active materials.

c. Relation of Voltage to Concentration.

Since the electrolyte, considered as a whole, does not change, it might be supposed that the electromotive force of the nickel-iron cell would be independent of the concentration. Such is very nearly the case. The researches of Foerster have shown that the reactions are not entirely independent of the electrolyte, however, and he has found changes of a few millivolts in the voltage of the cells when the specific gravity of the electrolyte is varied through limits wider than are ever found in practice. The effect of changing concentration on the voltage is therefore negligible.

d. Temperature Coefficient of Voltage.

The information contained in the literature on the temperature coefficient of voltage is conflicting. Schoop [36] quotes Foerster as saying that it is 0.0007 volt per degree. Foerster found it independent of the concentration of the electrolyte, as it should be theoretically if the reaction is independent of the concentration of the electrolyte. Thompson and Richardson,[37] on the other hand, found by experiment a temperature coefficient averaging 0.00024 volt per degree at the concentrations ordinarily employed, but with values of the coefficient that were higher for low concentrations, and lower for the higher concentrations.

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[36] Loc. cit.
[37] Trans. Am. Electrochem. Soc., 7, p. 114, 1905.

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CHAPTER V

CAPACITY

1. METHODS OF RATING STORAGE-BATTERY CAPACITY

a. Ampere-hour and Watt-hour Capacity.

The capacity of a storage battery may be expressed in two ways, either as the ampere-hour capacity or as the watt-hour capacity. The ampere-hour capacity is a measure of the electrochemical reactions taking place within the cell in accordance with Faraday's law. In this sense the term capacity means the quantity of electricity which the battery is able to deliver. The watt-hour capacity, on the other hand, is a measure of the energy or ability to do work. The relation of the ampere-hour capacity to the watt-hour capacity is a simple one. The watt-hour capacity is obtained by multiplying the ampere-hour capacity by the average value of the voltage during the discharge period. In stating the capacity of any battery, it is necessary to specify the rate at which the battery is to be discharged, the temperature and the final or cut-off voltage. It will be shown in this chapter that these three factors affect the capacity to a marked degree, apart from the effect of other factors which involve the design and condition of the battery.

The ampere-hour capacity of storage batteries is more often stated than the watt-hour capacity. It is simpler to measure; but a more probable reason for its almost universal use is the fact that in nearly all applications of storage batteries, the current requirement is an important and controlling factor. The torque exerted by a motor, the heating of a lamp filament, or the intensity of the field within a solenoid are proportional to the current. In such instances the current becomes a primary consideration and it is necessary to know the ampere-hour capacity. If the ampere-hour capacity and the number of cells in any battery are known, an approximation of the watt-hour capacity, sufficient for ordinary purposes, can be made immediately, since the nominal voltage of the lead-acid type of battery is 2 volts per cell and of the nickel-iron type 1.2 volts per cell.

b. Time and Current Ratings.

Batteries may be rated for ampere-hour capacity in several different ways. That most commonly adopted is the so-called time rating, by which the capacity of the battery is stated to be a certain number of ampere-hours which can be delivered within a specified time. For example, stationary batteries are rated at eight hours, and starting and lighting batteries are now rated at five hours and also at twenty minutes. The two ratings for the latter are given because of the dual character of the service which they render. Current ratings consist in specifying the capacity which may be obtained at some particular current. The time rating is to be preferred to the current rating because the time rating makes the capacities of different sizes of batteries comparable, whereas a current rating irrespective of the size of the battery imposes a less severe tax on the larger sizes and their capacity appears more than proportionately greater. A practical example of this is furnished in the case of starting and lighting batteries for automobiles. These have been rated in the past at 5 amperes; that is to say, the capacity of the battery was expressed as a certain number of ampere-hours which the battery was capable of delivering at a current of 5 amperes. A battery of this type whose cells contain seven plates has one-half the number of positive plates that a thirteen-plate battery would have, and the capacity of the former may naturally be assumed to be one-half the capacity of the latter, provided the details of structure, materials, and discharge are comparable. A comparison of the capacities of two such batteries at the 5-hour or any other time rate of discharge shows the ratio of capacities to be 1 : 2, but at the 5-ampere rate the capacities may be in the ratio 1 : 2.6.

The test current is easily found from the time rating. It is equal to the quotient of the rated capacity of the battery by the time.

c. Fluctuating and Intermittent Ratings.

The ampere-hour capacity of the battery is most easily ascertained when the current is constant during the period of discharge. In this case the ampere-hours are equal to the product of the current in amperes by the time in hours. If the current fluctuates with time, it is necessary to determine the integral

$$C = \int_0^t I dt$$

This can be obtained most conveniently by plotting the current as a function of the time and integrating the curve. The capacity C is

that obtained during a discharge lasting for a time t. In general t will be determined by the falling voltage of the cell, but it may be chosen as a purely arbitrary quantity.

Intermittent discharges often constitute the normal service that a battery may be called on to render. In such cases it is not unnatural that intermittent ratings should be given. For example, isolated plant batteries, in addition to having a continuous discharge rating of 8 hours, also have a second rating which is intermittent, covering a period of 72 hours.

d. Choice of End Points.

The entire theoretical capacity of a battery cannot be obtained, for several reasons. The electrolyte does not diffuse into the pores of the plates with sufficient rapidity when the pores are partially clogged with the lead sulphate; the resistance of the active material and the electrolyte increases as the discharge progresses; and, finally, it is not practical to discharge the battery to zero voltage.

As the battery discharges, the voltage at the terminals falls gradually from its open-circuit value, or slightly below, until the end of the discharge is approached, when it begins to fall much more rapidly. This point indicates that the exhaustion of the cell is near. If a curve is plotted, showing the voltage throughout the period of the discharge, the rapid fall begins at what is commonly known as the knee of the curve. The discharge may be continued slightly beyond this point, but only a small percentage of the total capacity can be obtained after the knee of the curve is passed. The amount of the actual capacity of the battery which remains after reaching the knee of the curve depends on the rate at which the battery is being discharged, the percentage being greater the higher the current. Standard practice has fixed some of the end-point voltages for discharges at various rates. For stationary batteries at the 8-hour rate this is 1.75 volts per cell. From this value the end-point voltages decrease as the discharge current increases, due allowance being made for the voltage drop in the cells and connectors because of their ohmic resistance. As an illustration of the variation of voltage with the rate of the discharge, the following figures for cells of the vehicle type are given for various multiples of the normal 5-hour rate of discharge.

TABLE XXXII

END VOLTAGES FOR CELLS OF THE LEAD-ACID TYPE

(The table applies primarily to vehicle cells)

Multiples of Normal Rate, 5 Hours	Volts per Cell
$\frac{1}{2}$	1.77
1	1.75
2	1.70
3	1.65
5	1.57
10	1.34

TABLE XXXIII

END VOLTAGES FOR EDISON CELLS

(The voltages are for various types and sizes of cells discharging at multiples of the normal rate, which for types A and B is 5 hours and for types G and J $3\frac{1}{3}$ hours.)

Multiples of Normal Rate	Volts per Cell
$\frac{1}{2}$	0.95
1	0.90
2	0.80
3	0.70
4	0.60
5	0.50

It is not economical to discharge the battery beyond the proper end point.

2. FACTORS DETERMINING CAPACITY

The principal factors which affect the capacity of storage cells are as follows: the amount of material within the cell, the thickness of the plates, the rate of the discharge, the temperature, the concentration of the electrolyte, the porosity of the plates, the design of the plates, and the previous history of the plates. These factors will be taken up, one by one, in the succeeding pages.

a. The Amount of Material within the Cell.

Application of Faraday's Law.—According to Faraday's law, 96,500 coulombs transform one equivalent of lead. Since the atomic weight of lead is 207.2 and the valence 2, the equivalent weight of lead is 103.6 grams. From this we may readily calculate the number of grams of lead, on the negative plate, that are transformed into lead sulphate during the passage of one ampere-hour. As 96,500 coulombs are equivalent to 26.80 ampere-hours, we have 3.866 grams of lead corresponding to 1 ampere-hour. Similarly, there are 4.463 grams of the peroxide, or active material of the positive plate, taking part in the reaction per ampere-hour. Two molecules of sulphuric acid in the electrolyte are transformed for each molecule of lead or lead peroxide, in accordance with the equation:

$$PbO_2+Pb+2H_2SO_4=2PbSO_4+2H_2O$$

The molecular weight of sulphuric acid is 98.076, and since the valence is 2, there are 98.076 grams of acid reacting for each equivalent of the lead. This amounts to 3.660 grams per ampere-hour. The net change in the weight of the electrolyte during charge or discharge differs from 3.660 grams per ampere-hour because of the formation of two molecules of water during discharge for each two molecules of the acid which take part in the reaction. When the battery is on charge the reverse takes place; that is, two molecules of water disappear for each two molecules of acid which are formed. The net change on discharge is, therefore,

$$-2H_2SO_4+2H_2O \rightarrow -2SO_3$$

This equation shows that the actual change in weight is 160.12 grams for every two gram-molecules taking part in the reaction. This loss in weight of the electrolyte is balanced by a corresponding gain in weight of the plates.

The mass of the electrolyte reacting at the positive plates during discharge is slightly greater than at the negative plates. This may be seen from the formula for the chemical reactions taking place at the positive and the negative plates, as follows:

At + $PbO_2+H_2+H_2SO_4=PbSO_4+2H_2O$

At − $Pb+SO_4=PbSO_4$

The actual consumption of sulphuric acid at the two plates differs more than the formula indicates, because it is necessary to take into account also the concentration changes caused by the migration of the hydrogen

(H^+) and the sulphate (SO_4^{--}) ions, and the formation of water at the positive plate. During discharge sulphate ions are consumed at both the positive and the negative plates. Sulphate ions migrate toward the negative plates and away from the positive plates. Hydrogen ions, on the other hand, migrate away from the negative plate toward the positive plate, where part of them are consumed in the formation of water. The net change taking place is therefore a greater loss of acid at the positive plate than at the negative. If this be considered together with the amount of water formed at the positive plate, it is found that the positive requires about 1.6 times the amount of acid that the negative plate requires during the discharge period. This fact is the principal reason for placing the corrugated side of the separators next to the positive plate in order to allow more space for acid. An interesting illustration of the necessity for the corrugations in the separator is furnished by tests which were made on small storage cells for signal purposes, in which the manufacturer had used thin wood separators without corrugations of any kind. It was found impossible either to charge or discharge the cell by more than a very small amount of its estimated capacity. It is sometimes noticed, when separators are renewed in old batteries of the starting and lighting type, that the capacity of the battery is considerably increased. This is undoubtedly due in part to the additional acid space provided next to the positive plates by new separators, since the ribs of the old separators are generally worn down almost to the web of the separator by the time that they require renewal.

Limitations to the Use of the Materials.—The foregoing figures showing the relation of lead, lead peroxide, and sulphuric acid consumed per ampere-hour are based entirely upon theoretical considerations. The practical amounts of the active materials required are considerably greater than those calculated from theory. There are several reasons for the limited use of the materials in actual service. The lead sulphate which is formed during the process of discharge is a non-conductor and increases the resistance of the active material of the plates. When the active material contains 50 per cent of sulphate the resistance has risen to a very high value. Another reason is the stoppage of the pores of the plates by the lead sulphate, which hinders the diffusion of the electrolyte. A third reason is the increasing resistance of the electrolyte itself. It was shown in Chapter III that the minimum resistivity of the electrolyte occurs at a specific gravity of approximately 1.225. As the specific gravity decreases below this point the resistivity increases, slowly at first, and then more rapidly as the concentration falls below 1.100. A fourth reason, which involves the design of the

plate itself, is the limited contact between the active material of the plate and its support. In the case of Planté plates, the support is the lead in the central portion of the plate itself. The support for pasted plates is the lead-antimony grid. The active material which is in immediate contact with the supporting material, and also in contact with the electrolyte, is in the most favorable position to take part in the reactions.

The ratio of the amount of active material taking part in the reactions to the total amount of active material present in the plates is called the coefficient of use. This coefficient differs markedly with the thickness and porosity of the plate, the rate of discharge and the temperature. A cell of good quality will have normally a coefficient of 0.25 or more. Lower values are to be attributed to deficient amount of electrolyte, lack of porosity of the plates, or improperly designed separators. Figure 57, from an article by Skinner,[1] shows the distribution of discharged material in plates of $\frac{7}{32}$ and $\frac{9}{64}$ inch thickness. The heavy shading in this figure indicates a high percentage of discharged material, while the light shading indicates little or no discharged material. From this figure it will be seen that the reactions of discharge penetrate into the plate only a portion of the way. For this reason, cells which contain thin plates are found to have greater capacity than cells of similar size containing thicker plates. This is particularly true at high discharge rates. Thin plates do not have a greater capacity *per plate* than thick plates. As a matter of fact, the capacity per plate is somewhat less, but owing to the larger number of plates that can be used in a cell of given size, the capacity of the cell as a whole may be considerably greater. For example, when two cells of equal size containing plates which are $\frac{14}{64}$ inch in thickness and $\frac{9}{64}$ inch in thickness are compared, it is found that the capacity of the thinner plate is 91 per cent of the capacity of the thicker plate, although one has only 64 per cent of the thickness of the other. In a given jar, therefore, there can be installed 56 per cent more of the thinner plates, and the relative capacity of the two cells, neglecting the effect of separators, can be calculated by multiplying 156 per cent by 91 per cent. This gives 142 per cent as the capacity for the cell containing thin plates, as compared with the capacity of the same cell with the thicker plates taken as 100 per cent.

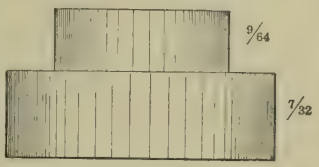


FIG. 57.—Distribution of discharged material determined by analysis and indicated as to the amount by the shading.

[1] Electric Vehicle Assoc., February 25, 1913.

The increase in capacity is, therefore, 42 per cent, which agrees very closely with laboratory measurements on such cells.

Maximum Output Obtainable.—The maximum output obtainable from storage cells can be computed. It is desirable to do this in order to determine how nearly the cells in common use approach the maximum possible output. It will be necessary to assume, for this estimate, thin plates of high porosity discharging at a low rate over a long period of time. The grid of a pasted plate amounts to 35 to 50 per cent of the weight of the finished plate, 50 per cent being a figure more commonly found than 35 per cent. It was found on page 179 that 3.866 grams of lead and 4.463 grams of lead oxide are required per ampere-hour. This is a total of 8.329 grams of active material as the theoretical requirement for each ampere-hour. We shall assume that the coefficient of use, as defined above, is 50 per cent. This is rather more than can ordinarily be obtained, even with soft plates, when discharging at the 5-hour rate. Dividing 8.329 grams by 0.50 gives 16.65 grams of active material as the best possible equivalent per ampere-hour. Assuming that the grid is only 35 per cent of the finished weight of the plate, the active materials will constitute 65 per cent and, dividing 16.65 by 0.65, we obtain 25.62 grams per ampere-hour as the weight of the plates. It is necessary now to ascertain the relation between the weight of the plates and the weight of the complete cell. This varies considerably among the cells made by different manufacturers, but in the following table are given the weight of each of the different parts of the cell in grams and the per cent of the total weight.

TABLE XXXIV

Relative Weights in Grams and Percentages of Various Parts of the Complete Cell

(Figures are for cells of the same size containing 15, 17 and 21 plates. The data for the 15 and 17 plate cells are the mean of three different makes; and for the 21 plate cells the mean of two different makes.)

Plates	Total Weight	Positives	Negatives	Yokes	Electrolyte	Wood Separators	Rubber Separators	Jar	Cover, Vent and Sealing Compound
Thick 15	21,237	7660	6657	982	4021	420	153	1150	194
	Per cent	36.1	31.3	4.6	18.9	2.0	0.7	5.4	0.9
Medium 17	21,528	7738	6203	1133	4561	403	269	1281	320
	Per cent	35.9	28.8	5.3	21.4	1.9	1.2	5.9	1.5
Thin 21	20,913	7077	5970	1240	4710	354	221	1187	154
	Per cent	33.9	28.5	5.9	22.5	1.7	1.0	5.7	0.7

In the table it is shown that the positive and negative plates constitute from 62 to 67 per cent of the total weight of the cell. Resuming the example, the weight of the cell per ampere-hour is therefore 25.62 divided by 0.624, or 41.3 grams per ampere-hour, as the result computed for the 21-plate cells. This corresponds to a maximum value of 24.2 ampere-hours per kilogram or 11.0 ampere-hours per pound of the cell. If we may assume that the average voltage during the discharge of the cell is 1.95 volts, the energy capacity becomes 47.2 watt-hours per kilogram or 21.4 watt-hours per pound. Lopp [2] has arrived at somewhat higher figures. He estimates the maximum practicable output to be 35.6 grams per ampere-hour or 28.1 ampere-hours per kilogram and 53.9 watt-hours per kilogram.

Having calculated the maximum output obtainable, we shall now compare it with the actual output of several different types of storage cells.

TABLE XXXV

THEORETICAL AND ACTUAL CAPACITY OF STORAGE BATTERIES

(Starting and lighting batteries (7-plate cells) discharged to 1.70 volts per cell at 5-hour rate and 1.50 volts at 20-minute rate, assuming the grid to be 50 per cent of the weight of the positive plates.)

Kind of Plate	Weight of Positive Active Material, Grams	Complete Theoretical Capacity, Ampere-hours	Actual Capacity 5-hour Rate, Ampere-hours	Coefficient of Use, Per Cent	Actual Capacity 20-minute Rate, Ampere-hours	Coefficient of Use, Per Cent
Soft.....	504	113	49	43	28	25
Medium.....	552	123	40	33	23	19
Hard.....	528	118	35	30	17	14
Very hard....	603	135	27	20	12	9

Batteries containing soft, medium, hard, and very hard plates have been chosen for this table. Column 2 shows the weight of the positive active material, since it is the positive plate which limits the capacity of the cell. Column 3 gives the complete theoretical capacity calculated on the basis of 4.463 grams of the peroxide per ampere-hour. In columns 4 and 6 is given the actual capacity of the battery measured at the 5-hour rate and the 20-minute rate. The remaining columns give the coefficient of use of the active material at these rates of dis-

[2] L'Indus. Electrique, March 25, 1904.

charge. The measured capacities are equivalent to 2.5 ampere-hours per pound per cell for the very hard plates and 4.5 ampere-hours per pound per cell for the soft plates, at the 5-hour rate of discharge. Special thin plate batteries of this type, designed for aeroplane service, have in some cases given as high as 6 ampere-hours per pound per cell at the same rate.

The output of storage cells of the vehicle type per unit of weight and space is given for the 5-hour rate of discharge in Table XXXVI. For this table, cells containing 15, 17, and 21 plates per cell have been chosen. The cells are, however, of the same external dimensions. The last figure given for the watt-hour capacity per cubic foot of the 21-plate cells indicates about 2 hp. per cubic foot of the space occupied by the battery.

TABLE XXXVI

OUTPUT OF STORAGE CELLS OF THE VEHICLE TYPE PER UNIT OF WEIGHT AND SPACE, 5-HOUR RATE OF DISCHARGE

(The cells were all of nominally the same external dimensions. The ampere-hours and watt-hours per unit of weight are based on the weight of a single cell. The watt-hours per unit of volume are calculated from observations on a battery of twelve cells. The plates were 21.9 cm. by 14.6 cm. ($8\frac{5}{8}$ by $5\frac{3}{4}$ inches).)

Number of Plates per Cell	Thickness of Positive Plates		Ampere-hours per		Watt-hours per			
	Cm.	Inches	Kilogram	Pound	Kilogram	Pound	$Dm.^3$	Cubic Feet
15	0.60	15/64	10.9	4.9	21.2	9.6	45	1263
17	0.52	13/64	11.7	5.3	22.6	10.5	48	1350
21	0.44	11/64	13.1	5.9	25.4	11.5	51	1440

As a third example, a certain stationary battery will be considered. This contains plates which are $10\frac{1}{2}$ by $10\frac{1}{2}$ inches. The projected area of the plate is therefore 110 square inches. The ratio of the developed surface of the plate to the projected area is 7 to 1 and, allowing for the two sides of the plate, the actual surface of the plate is computed to be 1540 square inches. If the cell contains six positive plates the total area will be 9240 square inches, or 59,600 square centimeters. The capacity of this cell at the 8-hour rate is found to be 480 ampere-hours, or 1 ampere-hour to 19.2 square inches (124 $cm.^2$) of plate surface. The complete cell weighs 232 pounds, and the output is, therefore, 2.06

ampere-hours per pound per cell. Assuming the average voltage on discharge to be 1.97, the watt-hour capacity is 945 and the watt-hours per pound 4.1, or 9 watt-hours per kilogram.

b. Thickness of the Active Material.

The capacity of a storage cell increases with the thickness of the active material of the plates at moderate rates of discharge, assuming that the plates have sufficient porosity for the electrolyte to reach the inner recesses. The effect of thickness cannot be considered apart from the rate of the discharge, because the faster the discharge the more nearly is the total output of the cell confined to the layers of active material that are in immediate contact with the free electrolyte. On excessively high rates of discharge, the output of the cell becomes practically a surface phenomenon. This is because there is insufficient time for the electrolyte to diffuse into the pores of the plates, and the sulphate forming at the surface clogs the pores. At low rates of discharge, on the otherh and, almost any depth of the active material

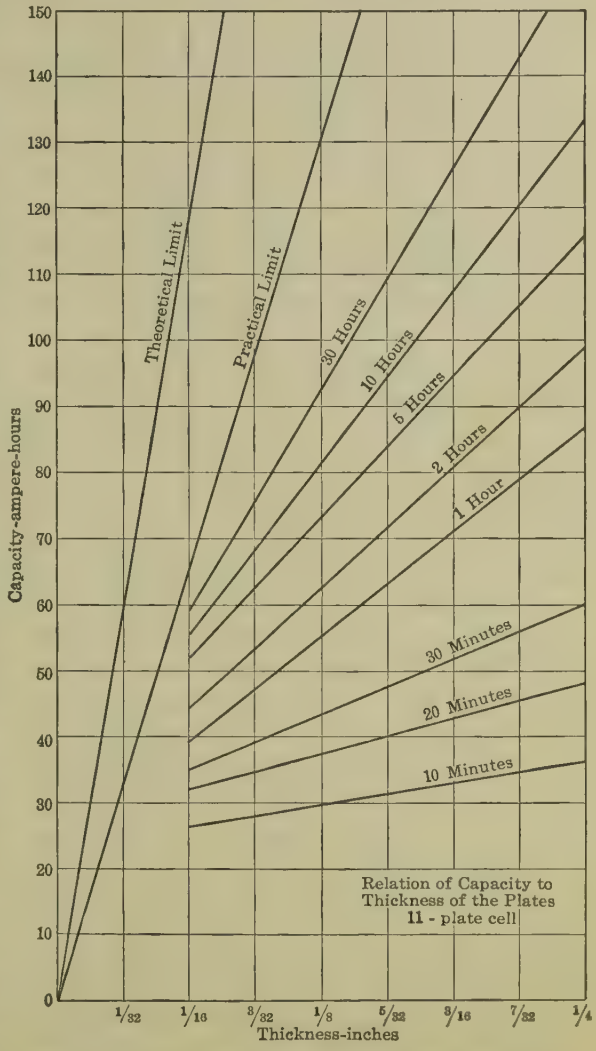


FIG. 58.—Dependence of capacity on thickness of the plates.

may become effective. For example, Table XXXVII and Fig. 58 show the relation of capacity to the plate thickness for a certain make of starting and lighting battery containing plates varying from $\frac{1}{16}$ inch to $\frac{1}{4}$ inch in thickness. These results are calculated for a battery containing 11 plates to the cell. The very great difference between discharges made at high rates and at low rates for plates of different thickness may be illustrated as follows:

> At the 10-minute rate of discharge, the $\frac{1}{4}$-inch plate gives only 38 per cent more capacity than the plate $\frac{1}{16}$ inch in thickness, but at the 30-hour rate it gives 170 per cent more.

TABLE XXXVII

VARIATION IN CAPACITY WITH THICKNESS OF PLATES

(Battery of the starting and lighting type containing eleven plates, $5\frac{5}{8}$ by 5 inches.)

Thickness		Capacity in Ampere-hours for Rates Indicated							
Inches	Mm.	10 Minutes	20 Minutes	30 Minutes	1 Hour	2 Hours	5 Hours	10 Hours	30 Hours
1/16	1.6	26.5	32.5	35.0	39.5	44.5	52.0	55.5	59.0
3/32	2.4	28.0	35.0	39.0	47.5	54.0	63.0	68.5	76.5
1/8	3.2	29.5	37.5	43.0	55.5	63.0	73.5	81.5	93.0
5/32	4.0	31.0	40.0	47.5	63.0	72.0	84.0	94.5	110.0
3/16	4.8	32.5	42.5	51.5	71.0	80.5	95.0	107.5	126.5
7/32	5.6	34.0	45.5	56.0	79.0	90.0	106.0	120.5	143.0
1/4	6.4	36.0	48.5	60.0	87.0	99.0	116.0	133.5	160.0

The negative plates are more sensitive to changes in thickness than the positive plates at low rates of discharge. This means that if the capacity of the positive and negative plates are equal at any high rate of discharge, the negative will exceed the capacity of the positive at any lower rate of discharge.

c. Area of the Plates.

In the preceding paragraphs a discussion of the amount of material in the cell and the thickness of the plates in relation to the capacity has been given. For any specified amount of material and thickness of the plate, the area of the plates is necessarily determined. The area is, therefore, not an independent factor in determining the capacity,

but since it is most easily measured, it is desirable to discuss the output in its relation to the surface of the plates. The area of the plate requires careful definition, since it may be taken to mean the area as calculated from dimensions of width and height, or the entire developed surface in the case of Planté plates, which is seven to ten times the area calculated from the dimensions. The area of pasted plates is calculated from the width and height and doubled to allow for both sides of the plates.

The output obtained from a given area of plate varies with the type of plate and the rate of the discharge. For Planté plates an output of 1 ampere-hour for each 100 to 125 square centimeters (15 to 20 square inches) of developed surface is about the average. The output for pasted plates of the vehicle type is shown in the following table:

TABLE XXXVIII

Output per Unit of Plate Area for Vehicle-type Cells of Nominally Same Size

Plates per Cell	Area Positive Group, Sq. Cm.	Capacity 5-hour Rate, Amp.-hrs.	Ampere-hours per	
			Sq. Cm.	Sq. In.
15	4480	228	0.051	0.328
17	5120	244	0.048	0.307
21	6400	260	0.041	0.262

It will be observed in this table that the capacity per unit of area is somewhat less for the thin plates than for the thicker plates. In the aggregate, however, the capacity for the thin plate cells is greater, because the increased surface of the plates more than offsets the decreased capacity per unit of area. The values given in the table are for vehicle cells discharging at the 5-hour rate.

In order to study the relation of plate area to the rate of discharge, reference is made to Fig. 58 in the preceding section, which is calculated for a cell of eleven plates. We shall take as an example a cell containing eleven plates, $\frac{3}{16}$ inch in thickness, and compare with it another cell of similar size having double the number of plates, which are $\frac{3}{32}$ inch in thickness. It is obvious that the volume of the plates in each case is the same, but that the area of the plates in the latter case is double that in the former. At the 30-hour rate, the cell containing the $\frac{3}{32}$-inch plates has an aggregate capacity of 152 ampere-hours. The cell containing the $\frac{3}{16}$-inch plates has a capacity of 127 ampere-hours. Halving the thickness of the plates, and thereby doubling the area, has increased

the capacity 20 per cent at this low rate of discharge. At the 10-minute rate of discharge, the cell containing $\frac{3}{32}$-inch plates has a capacity of 56 ampere-hours and the other cell with $\frac{3}{16}$-inch plates has a capacity of 33 ampere-hours. At this high rate of discharge, halving the thickness and doubling the area has increased the capacity of the cell 70 per cent. This example illustrates the importance of plate area, particularly in the case of batteries which are designed for discharge at high rates, such as those intended for starting and lighting service on automobiles and aeroplanes.

The effort to get great area of plates is found particularly in the case of aeroplane batteries, for which plates as thin as 0.050 inch are in some cases found. Thin plates possess two advantages for heavy service. The first is increased capacity for unit of space and weight. The second advantage is decreased resistance, which permits the cell to deliver very large currents with a small waste of energy within the cell itself. It is also possible to make use of separators cut from the more durable kinds of wood, in spite of their higher resistance because of the greater area. Batteries with thin plates possess one very great disadvantage, and that is the shortened life, or period of service, which they can give. At the present time, the demand for large capacity with the smallest possible amount of weight makes the use of these thin-plate batteries desirable on aeroplanes, but because of their short life they would not be considered satisfactory for other types of service.

d. Rate of Discharge.

It is a familiar fact that storage cells will not give as great capacities when discharging at high rates as when discharging at lower rates. The causes of the decreased capacity at the high rates are the following: the sulphation on the surface of the plates, which closes the pores; the limited time available for diffusion of the electrolyte; and the loss of voltage because of internal resistance of the cells.

Variation of Capacity with Time and Rate.—Figure 59 shows the discharge characteristics of one type of storage cell designed for starting and lighting service. The capacity is expressed as ampere-hours per positive plate, as a function of the current discharged per positive plate. That is to say, if a cell contains six positive plates, the ampere-hour capacity indicated for any given rate or time of discharge is to be multiplied by six. The capacities are shown for all rates of discharge, from the 3-minute rate to the 30-hour rate, but it should be noted that the scale of the abscissa is arbitrarily changed at 10 amperes per positive plate, in order to make it possible to show the complete characteristics of cells of this type within the limits of a single illustration. The diag-

onal lines intersecting the curve of capacities give the time of discharge. This figure applies to any battery containing any number of plates of the type to which this characteristic curve applies. The figure shows the capacity for any rate of current and for any time of discharge. It shows the time of discharge for any given current or delivered capacity, and the current for any given time or delivered capacity. It also shows

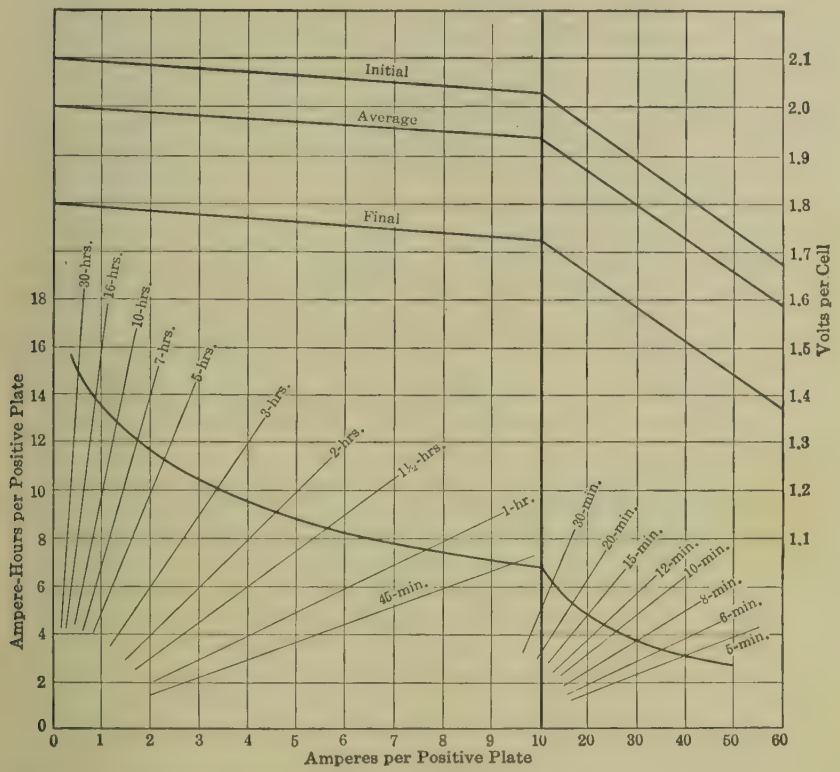


FIG. 59.—Discharge characteristics of a plate of the starting and lighting type.

the voltages, initial, average, and final, for any current rate or for any period of time. The watts or watt-hours for any current or time of discharge may readily be computed.

Successive Discharges.—The capacity of storage cells is seen from Fig. 59 to increase as the rate of discharge becomes lower. The physical significance of this effect lies chiefly in the diffusion phenomenon discussed in the paragraph on page 202. After a battery has been discharged to its final voltage at any given rate, it may be further discharged at any lower rate. That is to say, the total capacity of the

battery is equal to the summation of terms in accordance with the following equation:

$$C = \Sigma I_1 t_1 + I_2 t_2 + I_3 t_3 \ldots . I_n t_n$$

where I_1, I_2, I_3, etc., are successively lower values of the current, and the corresponding t's represent the time during which the battery was discharging at the rate indicated by I with the corresponding subscripts. Deception has in many cases been practiced upon automobile owners in order to sell special electrolytes for which extraordinary claims are made, by making use of the fact expressed in the equation above, the deception consisting in the failure to state that the same result may be obtained with the ordinary electrolyte as with the special product whose merits are exploited. A storage cell for demonstration purposes is discharged to the point where it fails to crank the engine, and then is allowed to rest for a period of a few minutes. During this time the more concentrated electrolyte in the cell is diffusing into the pores of the plates, and it is possible to discharge the battery again, the current, however, being somewhat lower on the average than in the preceding experiment. This may be repeated a number of times, and so it may appear, in the absence of exact measurements, that the battery has acquired an unlimited capacity because of the electrolyte which it contains.

Equations to Relate Current and Time.—A number of attempts have been made to develop equations which should relate the current to the time of discharge, in order that the capacity of batteries may be computed for any rate or time of discharge. The most widely used of these equations is Peukert's equation

$$I^n t = C \quad . . . . . (1)$$

In this equation, n and C are constants which may be evaluated by tests made on any cell or battery at two different rates of discharge. It will be assumed that the different rates are I_1 and I_2, the times of these discharges corresponding to t_1 and t_2. The values for n and C may therefore be calculated as follows:

$$\left.\begin{aligned} I_1^n t_1 &= C \\ I_2^n t_2 &= C \end{aligned}\right\} \quad . . . . . (2)$$

$$\left.\begin{aligned} n \log I_1 &= \log C - \log t_1 \\ n \log I_2 &= \log C - \log t_2 \end{aligned}\right\} \quad . . . . . (3)$$

$$n = \frac{\log t_2 - \log t_1}{\log I_1 - \log I_2} \quad . . . . . (4)$$

The numerical value for n being found for any particular type, the other constant C may be determined by solving either of the Equations (2).

Peukert's equation (Fig. 60) was derived and originally applied to bat-

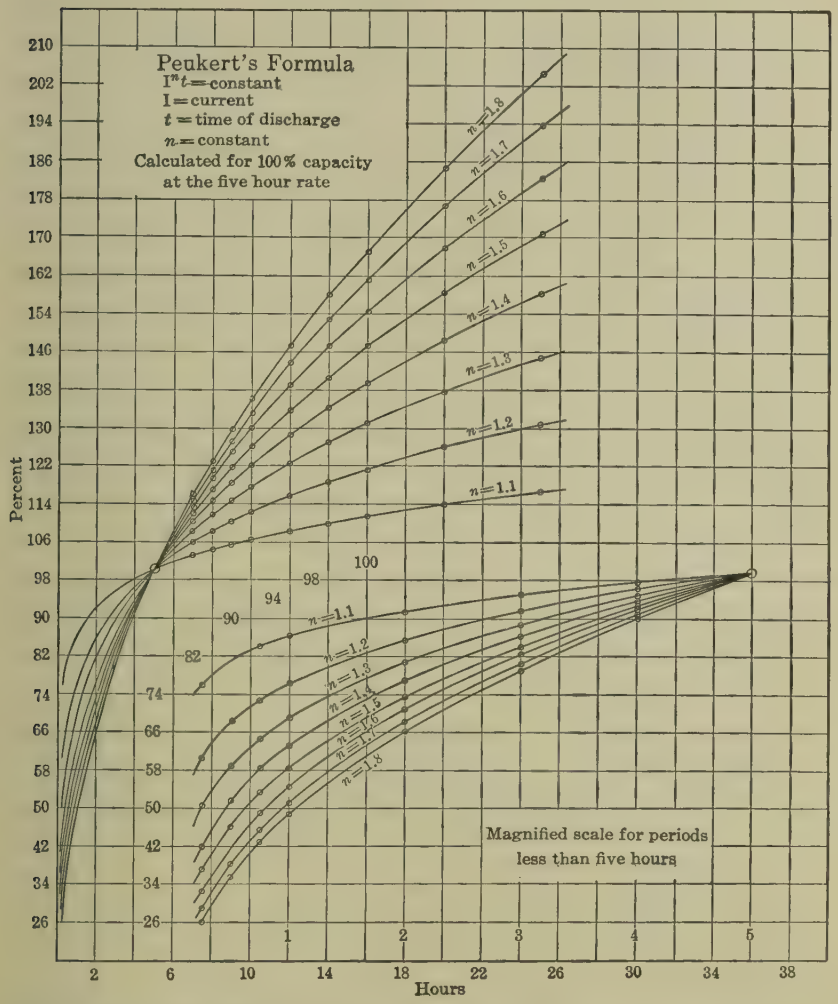


FIG. 60.—Capacity curves calculated from Peukert's formula and expressed as percentages of the capacity at the 5-hour rate.

teries made in European factories. This is true also of the other equations relating capacity and time of discharge, which will be discussed. It will be interesting, therefore, to apply Peukert's equation to an American-made battery of the starting and lighting type, since this battery is used

over a wider range of discharge currents than any other. The data on which the following example is based are taken from Fig. 59.

Example 1.—A battery of 15 plates of the type illustrated, containing 7 positive plates to the cell, is tested at the 5-hour and the 2-hour rates and the following data obtained. Required the values of n and C of Peukert's equation.

$$I_1 = 4.6 \times 7 = 32.2 \qquad t_1 = 2$$
$$I_2 = 2.3 \times 7 = 16.1 \qquad t_2 = 5$$
$$\log 5 = 0.699 \qquad \log 32.2 = 1.508$$
$$\log 2 = 0.301 \qquad \log 16.1 = 1.207$$
$$0.398 \qquad 0.301$$

$$n = \frac{0.398}{0.301} = 1.32.$$

Solving for C

$$C = (32.2)^{1.32} \times 2 = 195.6.$$

Example 2.—Using the values of n and C obtained in the preceding example, compute the length of time t of discharge for a 15-plate battery at 4, 20, and 100 amperes and compare the results obtained with the experimental data given in Fig. 59.

$$t = \frac{195.6}{(4)^{1.32}} = 31.4 \text{ hours; by the curve 33 hours.}$$

$$t = \frac{195.6}{(20)^{1.32}} = 3.75 \text{ hours; by the curve 3.74 hours.}$$

$$t = \frac{195.6}{(100)^{1.32}} = 0.45 \text{ hour; by the curve 0.41 hour.}$$

Other equations which have been suggested, to relate the capacity of the storage cells to the current at which they are discharged, are those of Schroeder [3] and Liebenow.[4] Schroeder's equation is

$$K\sqrt[3]{I^2} = m$$

K = capacity of the cell expressed in ampere-hours;
I = current rate of the discharge, and
m = constant.

This equation possesses an advantage in that it has only one constant, and it is therefore necessary to make only one discharge of any battery in order to compute the value of m and use the equation. However, the results calculated by this equation differ considerably from the

[3] Elektrotech. Zeit., p. 587, 1894.
[4] Zeit. f. Elektrochem., 3, p. 71, 1896.

experimental values obtained on cells of American manufacture. Liebenow's equation is

$$K = \frac{m}{1+aI}$$

This equation contains two constants, m and a, which may be evaluated from the results of two discharges on a storage cell at differing rates.

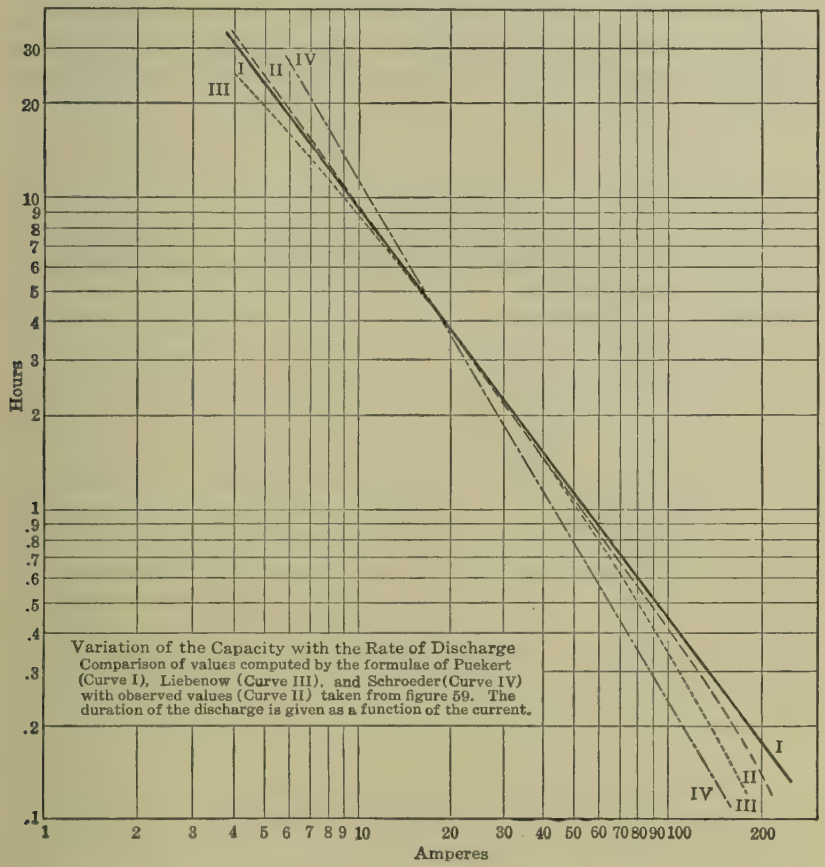


FIG. 61.—Comparison of observed capacities with those calculated from various formulæ.

In Fig. 61 is shown a comparison of the values computed by the equations of Peukert, Liebenow, and Schroeder, with the values as actually observed and taken from Fig. 59. The values for the current and time of discharge in Fig. 61 are given on a logarithmic scale, in order to permit of a wide range of current values. Curve 2 represents the values

actually observed. It will be seen that Curve 1, representing the results computed from the formula of Peukert, lies very close to the observed values. This affords a striking example of the validity and use of Peukert's formula. The capacities calculated from the formulas of Liebenow and Schroeder differ from the observed capacities by considerably more.

For purposes of hasty calculation, if the value of n for any given type of plate is known, Fig. 60 may be used. This shows the percentage capacities for cells discharging at time rates varying from 20 minutes to 25 hours, in terms of the capacity of the same cell taken as 100 per cent at the 5-hour rate.

e. Temperature.

The temperature plays an important part in determining the capacity which can be delivered by a storage cell under any specified conditions of rate and cut-off voltage. The temperature affects the capacity of storage batteries, first, because it decreases the resistance of the electrolyte as the temperature increases; second, because it raises the voltage as the temperature is raised; and third, because it increases the rate of diffusion of the electrolyte into the pores of the plate.

The electrolyte between 18° and 25° C. (64° to 77° F.) for 1.300 acid decreases in resistivity by 0.026 ohm-centimeters per degree. In Chapter III a table has been given from which the changes in resistivity for any concentration can be calculated. In the following table the resistivities for acid of 1.300 sp. gr. over the working range of temperatures from +40° C. (104° F.) down to −18° C. (0° F.) are given, because they show how great is the increase of resistivity as the temperature is lowered. The resistivity at −18° C. is nearly three times that at the higher temperature.

TABLE XXXIX

Resistivities within Working Range

° C.	° F.	Resistivity (Ohm-Cm.)
40°	104°	0.89
25°	77°	1.28
18°	64°	1.46
0°	32°	1.92
−18°	0°	2.39

The effect of temperature on the open-circuit voltage of the storage cell is very small, and for all ordinary purposes may be neglected within the range from $-18°$ C. to $+40°$ C. The increase in voltage for cells containing electrolyte of 1.300 sp. gr. is 0.023 volt. The temperature coefficient of voltage of a storage cell has been discussed in Chapter IV.

Increase in temperature is accompanied by an increase in diffusion of the electrolyte. This is probably the most important factor that accompanies changes in temperature. The diffusion of the electrolyte depends in part on the viscosity of the solutions. The viscosity of a solution of specific gravity 1.200 is only half as great at 40° C. (104° F.) as it is at 15° C. (59° F.). Data appear to be lacking to show what the viscosity of these solutions may be at the lowest temperatures encountered by storage batteries, but the marked change over the range of 25° suggests that this effect is very large. The matter of diffusion is discussed more at length in the section on porosity.

Temperature Coefficient of Capacity.—Many experiments have been made to determine the temperature coefficient of capacity of storage cells. The value 1 per cent per degree Centigrade (0.56 of 1 per cent per degree Fahrenheit) for cells containing Planté plates is a value which has been given in the books by Schoop, Wade, and Liebenow.[5] Liebenow states that he found the capacity to be a linear function of the temperature, and the increase for 1° rise in temperature to be 1 per cent of the capacity at 15° C. In Fig. 62 is given a curve showing the variation of capacity with temperature for cells of the lead-acid type containing pasted plates, which represents the mean results of tests obtained from cells of three different manufacturers. The agreement between the results of these different manufacturers is surprisingly good, and it is believed that this curve may reasonably represent any type of pasted plate battery for starting and lighting service with an electrolyte having a specific gravity 1.280 to 1.300. One hundred per cent capacity is given for a temperature of 25° C. (77° F.). If it is desired to use another temperature as standard, it is possible to displace the curve parallel to itself along the x-axis. This figure shows that between $+20°$ C. and $-20°$ C. the change in capacity per degree Centigrade is 1.34 per cent, corresponding to 0.75 per cent per degree Fahrenheit. Above 20° C. the value is somewhat less. Between $+20°$ and $+45°$ C. the coefficient averages 0.77 per cent per degree Centigrade, or 0.43 per cent per degree Fahrenheit.

Variation of the Coefficient with the Rate.—The data given in Fig. 62 apply to discharges which are made at the 5-hour rate. Since

[5] Dependence of Capacity on Current Strength, Inaug. Dissert., Göttingen, p. 6, 1905.

the temperature affects the rate of diffusion, it may be readily suspected that the temperature coefficient will vary with the rate of discharge. This is found to be the case, and Fig. 63 shows the values in per cent per degree for both the Centigrade and Fahrenheit scales, for discharge rates of 8 hours or less. This figure shows that the temperature coefficient at the 8-hour rate of discharge is almost exactly 1 per cent per

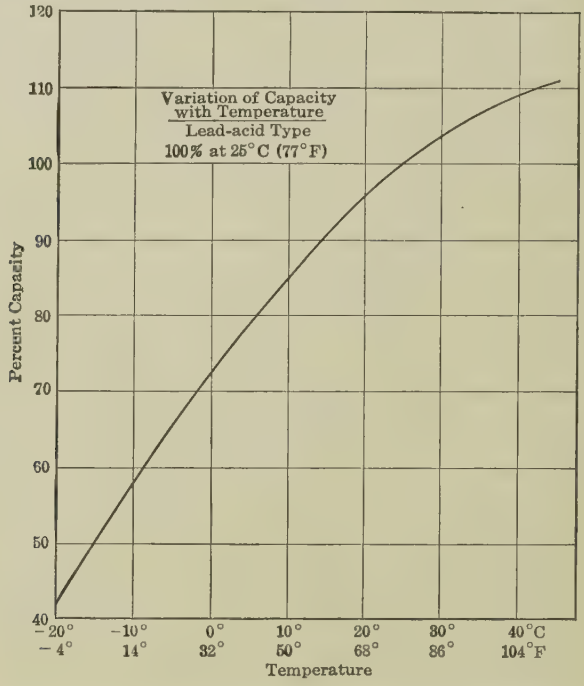


Fig. 62.—Effect of temperature on capacity expressed as percentages of the capacity at 25° C.

degree Centigrade, in accordance with the statements made in the books previously published. At the 20-minute rate of discharge, however, the factor is in excess of 1.8 per cent per degree Centigrade, or almost double that at the 8-hour rate.

f. Concentration of the Electrolyte.

Change in Capacity with Concentration.—The concentration of the acid in the pores of the plates is vital in determining the voltage and the capacity. Unless a sufficient amount of sulphuric acid can be maintained in the pores during discharge, the voltage at the terminals

of the cell will decrease rapidly and the cell will become exhausted. The concentration affects the capacity, first, because it determines the potential of the plates; second, because it affects the resistance of the electrolyte to the passage of the electric current; third, because it affects the viscosity of the electrolyte and thereby the rate of diffusion; fourth, because differences in the concentration of the electrolyte in the pores of the plates and outside also affect the rate of diffusion.

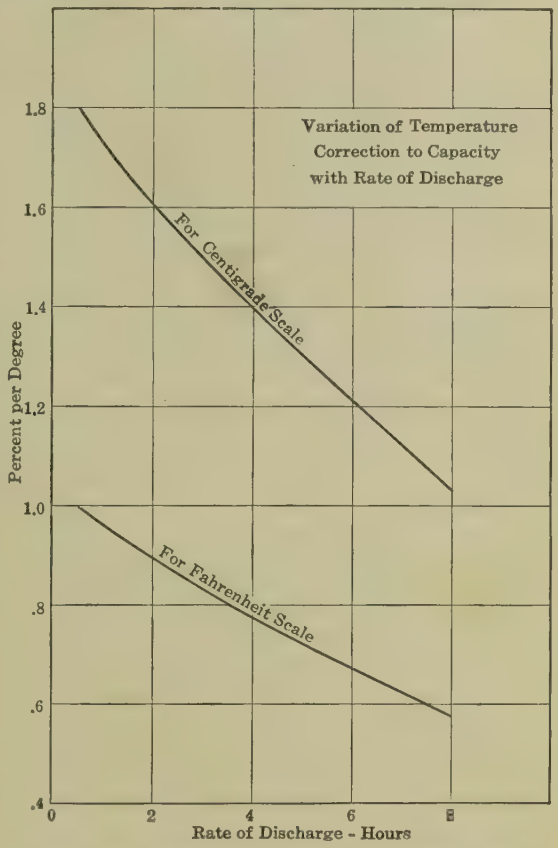


FIG. 63.—Effect of the rate of discharge on the temperature correction.

Liebenow's Experiment.—Liebenow[6] carried out a celebrated experiment which has often been quoted to show the influence of concentration on the capacity of the plates. He welded a negative plate of the pasted type to form a window in the side of a lead vessel which he then placed in a larger vessel. By varying the height of the electrolyte in the two vessels, it was possible to exert a hydrostatic pressure to force the electrolyte through the plate, which served as a window of the inner compartment, in either direction, or, if the electrolyte were at the same level in the two vessels, to eliminate the hydrostatic pressure. Liebenow suspended a positive plate inside of the inner vessel and determined the capacity of this arrangement when the electrolyte had the same level in the two vessels. The capacity was found to be about 14 ampere-hours. After this the level of the electrolyte in the

[6] Zeit. f. Elektrochem., 4, p. 61, 1897.

inner compartment was maintained higher than in the outer vessel, so that the acid was continually passing through the plate. He again determined the capacity and found it to be approximately 42 ampere-hours, or three times as great. This experiment shows that if the concentration of the electrolyte in the pores of the plate can be maintained during the discharge period, the cell will have a much greater capacity. In other words, the capacity of the cell in the ordinary case is limited by the supply of electrolyte. Only in extreme cases, when the discharge takes place at very low rates and the coefficient of utilization of the active material is very high, can the capacity be said to be limited by the amount of active material available.

Maximum Capacity.—Experiments to determine the concentration of electrolyte for which the capacity of any given storage cell is a maximum have been made by numerous observers. Their conclusions have varied from concentrations of 1.100 to 1.270 sp. gr. The wide divergence in their results is probably caused by their taking insufficient account of the conditions of the experiments. Some experiments have been on pasted plates and others on Planté plates. The current densities have doubtless differed greatly. In some cases the concentrations are the final densities, and information is not available to show what the initial values were. There is little to be gained, therefore, in a tabulation of these results.

The capacity of the cells increases as the specific gravity increases, within the range now employed. This is particularly true at high rates of discharge and when the capacity of the cells is limited by the positive plates. Figure 64 shows a series of experiments made on small cells of the couple type having pasted plates and containing electrolyte of specific gravities ranging from 1.080 to 1.310 at the beginning of the discharge. The figure shows the characteristic curves for discharges at 4 amperes and 1 ampere. The plates were 3 inches wide by 4 inches high. This figure shows that when the rate of discharge was decreased from 4 amperes to 1 ampere, the time of discharge for the cell containing the highest specific gravity was increased 6.4 times, but the cell containing the lowest specific gravity gave 35 times the length of discharge at the lower current rate. This figure illustrates the very great influence which the concentration of the acid has on the capacity of the cell, particularly for discharges at high rates.

The relation of concentration to maximum capacity includes the following factors:

(1) The resistivity of the electrolyte is a minimum if the specific gravity is 1.225.

(2) The self-discharge of the negative plates increases very rapidly

when the specific gravity is above 1.250. This factor ordinarily does not appear in the operation of the storage cells because the positives, rather than the negatives, limit the capacity.

(3) The final specific gravity, rather than the initial specific gravity, is the important factor, since the final specific gravity determines the rate of diffusion at the end of the discharge. In present-day practice, cells are operated over a great range of specific gravities, and because of the limited space, it is necessary that the initial specific gravity should be high in order that the final specific gravity may not be too low.

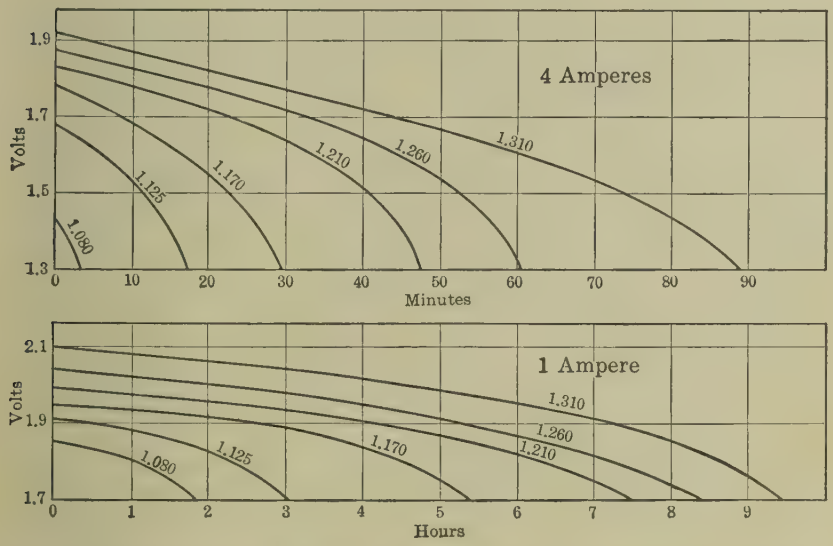


FIG. 64.—Effect of the concentration of the electrolyte on the capacity of cells discharging at 1 and 4 amperes.

(4) The maximum capacity moves to the higher concentrations as the rate of discharge increases. This factor was shown very clearly by Jumau.[7] His experiments indicate that the influence of concentration is greater for the positive plates than for the negative. There appears to be no reason to account for the relatively low value of the maximum capacity of negative plates other than the local action which sets in when these plates are immersed in solutions of high concentration. The best-made plates of the present day, however, are probably less subject to this effect than those made in the past. One reason why the positives require a higher density of acid is that water is formed at the positive

[7] L'Ecl. Electr., 18, p. 201, 1899.

plate as a part of the reaction during discharge. For every gram-molecule of lead peroxide which is transformed, two gram-molecules of water are formed, and this dilutes the electrolyte in the pores.

g. Porosity of the Plates.

The importance of porosity of the plates in facilitating the access of electrolyte to the active material on the positive plate has been treated in connection with other factors previously discussed. The porosity of the finished plate varies with the material from which it was made and with its state of charge. The aggregate porosity of the plate is a matter of 50 per cent of the entire volume of the plate, but the individual pores are probably little more than molecular in size.

While the term porosity is generally understood to indicate the possession of absorption qualities similar to those of a sponge, it is desirable to establish a definition for porosity. The porosity is equal to 1 minus the ratio of the apparent density of the active material to the real density. From this definition the percentage of porosity of the plates may be obtained in any case by multiplying by the factor 100.

Variation of Porosity with State of Charge.—The porosity of the plate varies with the state of charge. Lead sulphate, which is formed as a product of the discharge of the cells, is less dense than either lead or the oxide of lead. It, therefore, occupies more space than the active materials, yet the apparent volume of the plate does not change. The reason for this is that the expansion is taken care of by the pores of the plates. If the discharge is greatly prolonged, however, beyond the customary end points, the amount of sulphate formed may become so great that the pores of the plate are no longer adequate to supply room for it. Then the active material bulges or is pushed out altogether from the plate. The difference in porosity of the active material in the charged and discharged condition was demonstrated by experiments made by Duncan and Wiegand.[8] They determined the amount of acid diffusing from the pores of plates in the charged and discharged conditions, and found that the amount of acid diffusing from a given plate was twice as great when charged as when discharged.

Measurement of Porosity.—The relative porosity of storage-battery plates can be determined by the amount of water that can be absorbed by the pores when they are in the dry condition. Such a measurement, however, is seldom accurate, and it is preferable to determine the actual porosity by calculation as follows:

[8] Trans. Amer. Inst. Elec. Engrs., 6, p. 217, 1889.

Example:—Determine the porosity of a positive plate of an aeroplane battery. The three dimensions are as follows:

Length	12.46	cm.
Width	14.28	cm.
Thickness	0.1275	cm.

(In order to obtain a sufficiently accurate determination of the thickness, it is necessary to use a micrometer caliper and to take the mean of a number of readings at different parts of the plate.)

The volume of this plate is 22.632 cm. To this must be added the volume of the lug, 1.03 cm. The total volume of the plate is 23.662 cm. The volume of the grid equals the weight of the grid divided by its density. Its density is determined by Table II, given in Chapter II, after a chemical analysis has been made to find the percentage of antimony which it contains. In this example the volume of the grid equals 81.215 divided by 1.085, =7.485 cu. cm. Deducting the volume of the grid from the volume of the plate, we obtain the space available for the active material, 23.662−7.485=16.178 cu. cm. The weight of the fully charged plate washed and dried was 143.3 grams. Deducting the weight of the grid, 81.22, the weight of the active material is 62.08 grams. The actual volume of the active material is equal to the weight divided by the density, =62.08 divided by 8.8, =7.06 grams. The pores of the plate are equal to the space available for the active material minus the actual volume of the material, =16.18−7.06=9.12 cu. cm. The porosity equals the ratio of the pore space to the total space available for active material=56.5 per cent. *Answer.*

A determination of the porosity of the same plate by the absorption method, the water being drained off for about one minute, gave the porosity as 50.5 per cent. The porosity as determined by water is consistently less than the calculated value because of the rapid evaporation of the water on the surface of the plates and the capillary action of the pores. Determining the porosity of the negative plates requires a special procedure, because the negative plates in the battery oxidize spontaneously when exposed to the air, accompanied by a marked rise in temperature. Fully charged negative plates have been successfully dried without oxidation or heating, at the Bureau of Standards, by the following procedure:

The plates, after being completely charged, were immersed in distilled water which had been boiled to expel the dissolved air, and then washed in successive changes of this water until no trace of sulphates could be detected, following which the plates were dried in a vacuum. Negative plates prepared in this way present a bright blue appearance which is in marked contrast to the ordinary gray color of the negative plate.

When a storage battery discharges, the lead sulphate tends to form at the mouth of the pores. If the discharge is made at a very high rate, the formation of sulphate becomes almost entirely a surface phenomenon and the surface of the plate is incrusted with the sulphate, which hinders

the free access of electrolyte to the active material. This clogging of the pores naturally limits the available capacity of the cell. When discharges are made at low rates there is less tendency for the sulphate to form on the surface exclusively, and there is opportunity, therefore, for the electrolyte to diffuse into the pores during the discharge.

Very porous plates are less sensitive to changes in the current strength, for the reason that the pores do not become so quickly clogged with lead sulphate.

Diffusion Phenomena.—The diffusion which takes place during both the charging and discharging periods is a most important factor in the operation of the cell. According to the kinetic theory of diffusion, the molecules and ions in the electrolyte are in continual motion. The proof of this theory is found by examination of colloidal solutions in which the Brownian movement of the colloidal particles can be clearly seen. The motion of the particles to and fro is resisted by the viscosity of the solution.

Fick's law states that the rate of diffusion varies as the difference in the concentration and as the area of the pores, and inversely as the length of the path to be traveled. We may, therefore, write the equation for the amount of acid diffusing in a given time as follows:

$$Q = D\Delta C\frac{a}{l};$$

Q = quantity of acid diffusing in a given time;
D = diffusion coefficient;
ΔC = difference in concentration between the electrolyte within the pores and that outside;
a = aggregate cross-section of the pores, and
l = distance through which the acid must diffuse.

D is a most important and significant factor in this equation, but it is by no means simple. In order to obtain a definite idea concerning the process of diffusion, it is necessary to make application of gas laws to the electrolyte, since the phenomena of the diffusion of gases has received more extended study. Sutherland [9] has given a a formula for D as follows:

$$D = \left(\frac{RT}{N}\right)\left(\frac{1}{3\pi\eta d}\right)$$

R = gas constant;
T = absolute temperature;

[9] Phil. Mag., 9, p. 781, 1905.

N = Avogadro constant;
η = vicosity of the solution, and
d = diameter of the diffusing particles.

The most significant terms in this equation are those for the temperature and the viscosity. The equation states that the rate of diffusion depends on the absolute temperature and inversely on the viscosity.

The viscosities for solutions of sulphuric acid of the specific gravities which are used in batteries are given in Table XVI in Chapter III. This table shows that the viscosity of solutions having a specific gravity 1.300 is practically double that for solutions of 1.100. The viscosity decreases as the temperature increases. At 45° the viscosity is only half of its value at 15° C. Unfortunately, no data are available for the viscosity at temperatures lower than 0° C.

The displacement of acid as a result of the diffusion process into the pores when the battery is discharging and out from the pores when the battery is charging is a controlling factor. Einstein has deduced a formula for displacement, which is as follows:

$$X = \sqrt{2Dt}$$

In this equation
X = distance through which the displacement takes place;
D = diffusion coefficient as given above, and
t = time.

Combining this equation with the preceding one and substituting known values for R, T, and N, we may eliminate D and obtain an expression given in a paper by Wells and Gerke [10] as follows:

$$t = \frac{X^2 d}{4.7 \times 10^{-11}}$$

From this equation it appears that the time required for the acid to travel a given distance increases as the square of the distance. The diffusion process is therefore a slow one when the diffusion has to take place through any considerable thickness of the active material. Although this equation has been derived from laws governing the diffusion of gases and applied to the movement of colloidal particles, it nevertheless gives an insight, in a qualitative way at least, into the diffusion process in liquids. It explains why so thin a layer of the active material actually takes part in the reactions and why the capacity is increased as the rate of discharge is decreased. If the ions and molecules were not very small, diffusion of the electrolyte would be an extremely slow process.

[10] Journal American Chemical Society, 41, p. 312, 1919.

Other phenomena related to diffusion deserve mention, although they affect the operation of the cell to a very small extent. Electrical endosmos undoubtedly takes place through the porous separators during both charge and discharge. It does not occur within the porous sections of the plates, however, because the active material of the plates is an electrical conductor, and therefore the potential differences are small in spite of the difference of concentration of the electrolyte in the pores of the plates and outside. There is an electromotive force at the liquid junction between the two concentrations. This is caused by the unequal speed of the ions. The hydrogen ions move the most rapidly, carrying with them positive charges. Since the electrolyte in the pores of both positive and negative plates becomes depleted on discharging, the liquid-junction potentials are in opposite directions at the two plates and nearly equal in magnitude. Hence their combined effect is negligible. For a discussion of liquid-junction potentials, reference is made to Clarke.[11]

h. Previous History of the Plates.

Variation of Capacity During Life.—When the plates in a storage battery are new, there is an increase in the capacity during the first

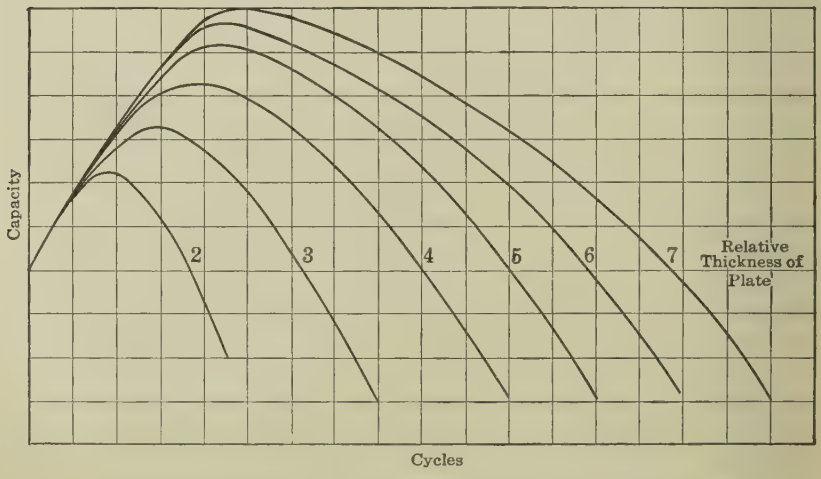


Fig. 65.—Relative life and capacity of plates of varying thickness.

few cycles of charge and discharge, up to a maximum value beyond which the capacity gradually falls off. Thin plates reach their maximum capacity after a smaller number of cycles than thick plates, but beyond

[11] Determination of Hydrogen Ions, p. 112, 1920.

this point their decrease in capacity is more rapid. The variations in capacity during the life history of the plates are shown for several relative thicknesses of plate in Fig. 65. The curves of this figure should be regarded as qualitative, designed to show the relative number of cycles for plates of a particular type. Thin plates of one manufacturer may be superior to equally thick or even thicker plates made by another manufacturer. After the capacity of the plates has fallen to 80 per cent of their initial capacity, they are considered worthless. During the later cycles in the life history of the plates, the decrease in capacity of the negative plates is caused primarily by a decrease in the porosity of the material or shrinkage of the plate itself. The loss of capacity of the positive plates is caused by the loosening of the active material. In addition to these effects, however, there is a third effect arising from the wearing of the separators. As the separators become thinner and thinner, particularly the ribbed portions, the space available for the electrolyte next to the positive plate becomes inadequate, and the capacity of the cell may be limited by insufficient acid for the action of the positive plate.

TABLE XL

HYSTERESIS EFFECT

Average measurements on four thin-plate batteries showing the variation of capacity with changes in the rate of discharge.

Rate of Discharge	Ampere-hour Capacities	
	Batteries 1 and 2	Batteries 3 and 4
5-hour rate	31.5	65.9
20-minute rate	17.8	41.6
Subsequent discharges at this rate	15.0	31.7
5-minute rate	6.9	14.7
Subsequent discharges at this rate	6.1	13.0
20-minute rate	13.7	32.2
Subsequent discharges at this rate	....	....
5-hour rate	30.8	63.9
Subsequent discharges at the 5-hour rate	31.6	64.6

Effect of Previous Discharges.—The capacity of the plates is affected by the discharges immediately preceding. For this reason it is desirable, in making tests, to run a few preliminary cycles at the same rate of discharge as is to be used in the formal test. This hysteresis effect was observed by Jumau [12] and has been confirmed at the Bureau of Standards. Jumau found that the capacity delivered at any given rate depends on the previous discharge. The capacity is lower if the discharge has been preceded by a discharge at a higher rate, and it is higher if preceded by a discharge at a lower rate. This effect, although small, is nevertheless of importance in makng tests. Table XL gives measurements on thin-plate aeroplane batteries illustrating this effect. There is also a sluggishness which is caused by inactivity for any considerable period of time. This may be overcome by charging and discharging the cells for a few cycles.

Effect of Purity of the Materials.—A third effect influencing the capacity is the purity of the materials of which the plates are made. If small traces of copper and iron are present in the paste, they will gradually pass into solution and affect the capacity as a result of local action. It not infrequently happens that when the electrolyte of new cells is tested after only a few cycles of charge and discharge, the amount of impurities found in solution may be considerably less than if the test for purity were deferred for a longer time.

Period of Standing.—It is, of course, obvious that the charging must be adequate if the battery is to deliver its capacity satisfactorily, particularly if a long period of time is to elapse between the charge and the discharge. The rate at which the battery is charged is of little moment in its effect upon the capacity, provided the total amount of charge is sufficient.

3. CAPACITY OF EDISON BATTERIES

a. Rating.

The Edison batteries of all sizes are normally rated at the 5-hour rate of discharge. The capacities for standard types and sizes of plates have been given in Table IX at the end of Chapter II.

The end-point voltages to be observed in making discharges are given in Table XXXIII in terms of multiples of the normal rate of discharge for the various types of Edison batteries.

b. Amount of Material within the Cell.

As in the case of the lead-acid batteries, the capacity of the Edison batteries is dependent on the amount of active material within the

[12] L'Ecl. Electr., 16, p. 413, 1898.

individual cells. The amount of nickelous hydroxide which is used in filling the tubes averages 4.64 times the amount theoretically required. Assuming the oxide of nickel, NiO_2, to be the highest reaction product and the nickel hydrate, $Ni(OH)_2$, expressed as the hydrated oxide, $NiO \cdot H_2O$, to be the lowest, the reaction may be expressed by the equation:

$$NiO + O = NiO_2$$

Since the electrochemical equivalent of oxygen is 0.2984 gram per ampere-hour, it may readily be calculated that 1.3932 grams of NiO are required for the reaction. The NiO is equivalent to 124.12 per cent of its weight of the nickel hydrate and, therefore, the amount of the nickel hydrate theoretically rquired is 1.729 grams per ampere-hour. Actually the amount necessary is much greater than this.

Representing the reaction at the negative plate by the equation

$$Fe + O = FeO$$

the theoretical amount of iron required per ampere-hour is calculated to be 1.042 grams. The actual amount necessary averages 5.78 times this amount. The active material of the negative plate contains about 40 per cent of metallic iron when fully charged. This oxidizs spontaneously, reducing the available capacity. For this reason it has been found advisable to allow the batteries to stand in a partially discharged state rather than fully charged when it is desired that reasonable activity be available after a protracted stand.

The electrolyte of the nickel-iron type of battery does not change in chemical composition or density (considered as a whole) during charge and discharge, because the reactions at the electrodes are only oxidation and reduction of the active materials. As will be shown later, the discharge of these batteries is terminated because of the exhaustion of the active material of the positive plate, and not because of lack of electrolyte in the pores, as in the case of the lead-acid type of battery. The capacity of the cell is independent of the amount of electrolyte that it contains.

c. Thickness of the Plates.

The A type of plate for Edison cells contains thirty tubes which are $\frac{1}{4}$ inch in diameter. The G type of plate having the same length and width contains forty tubes which are $\frac{3}{16}$ inch in diameter. The ratio of capacity of the G plate to the A plate is 25 ampere-hours to $37\frac{1}{2}$ ampere-hours. From this it is evident that the capacity of the thinner

plate is considerably less. Comparing equivalent sizes of cells, however, the type A 6 and its equivalent G 9 of the same external dimensions both have the capacity 225 ampere-hours. The object of thin plates in the Edison battery is, therefore, not to increase the capacity, as was the case with lead batteries, but to reduce the internal resistance for certain types required for heavy duty.

d. Effect of the Rate of Discharge.

The relation of capacity to the rate of discharge of Edison cells is quite different from that of the lead-acid batteries. The full capacity of an Edison battery may be obtained, irrespective of the rate of the

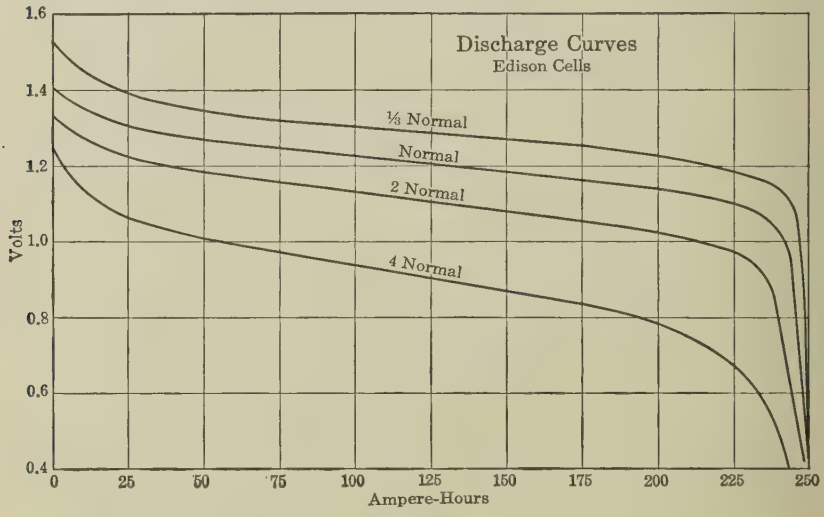


Fig. 66.—Discharge curves of Edison cells at various rates, type A6.

discharge, but at a lower voltage. This effect is shown by the curves of Fig. 66 which apply to a cell of the type A 6 discharging at 15, 45, 90, and 180 amperes. It will be observed that the capacity delivered at 180 amperes is approximately the same as the capacity at 15 amperes, but the voltage at the terminals of the cell is very much lower. Two reasons may be assigned for this peculiar effect. The active material of the positive plate, which limits the discharge of an Edison cell, contracts during discharge. The pores of the plate are thus expanding during the discharging process and allow free access of the electrolyte to the material. There is nothing analogous in the operation of the Edison plate to the formation of sulphate which clogs the pores of the lead batteries. Although Edison batteries can deliver their full ampere-

hour capacity even at high rates of discharge, there are practical limitations which make this effect of less importance than would otherwise appear. In operating the motor on a truck, for example, it is necessary that the voltage at the terminals of the battery should be maintained at a certain minimum value if the truck is to maintain its speed. If arbitrary end voltages be assigned, it will be found that the capacity of the Edison batteries to those voltages decreases as the rate of discharge increases, in much the same way as was found with the lead batteries. The watt-hours delivered at high rates of discharge decreases as the rate of discharge increases because of the fall in the average voltage.

e. Effect of Temperature.

The capacity of Edison batteries is decreased as the temperature is decreased. The relation does not, however, follow a nearly linear law as in the case of lead batteries. The Edison batteries have a critical temperature which varies with the rate of the discharge. Below this critical temperature the output is small; above it, practically the full capacity of the battery may be obtained. Comparatively little information is available on this subject, but a paper by Holland [13] gives data for cells of the type A 6 discharging at currents ranging from 15 to 75 amperes. The normal rate of discharge for this size of cell is 45 amperes. At the normal rate the critical temperature is in the neighborhood of 5° C. (41° F.). For rates of discharge in excess of this, the critical temperature is higher, and for smaller rates it is lower. This does not mean that Edison batteries cannot be used at temperatures below the critical temperature. The ohmic resistance in cells of this type is so great that the heat which is liberated within the cell, equal to the product I^2R, is enough to warm the cell appreciably and keep it above the critical temperature under the ordinary conditions of operation. The cell will be operative although used in a temperature much below the critical value, provided the temperature of the electrolyte within the cell does not fall below the critical value.

f. Concentration of the Electrolyte.

The concentration of the electrolyte in the Edison cell is of comparatively little importance. The concentration does not change during the charging and discharging of the cell but falls gradually over a long period of time. This decrease undoubtedly affects the rate of diffusion as well as increasing the resistivity. It is therefore con-

[13] Central Station, 11, p. 135, 1911.

sidered advisable to renew the electrolyte when it has decreased to certain values as indicated in Chapter III.

g. Previous History of the Plates.

The previous history of the plates affects the capacity of Edison batteries in much the same way as is found in the case of lead batteries. Sluggishness occurs when the battery is allowed to stand idle for a considerable period of time. This sluggishness is caused by the slow oxidation of the iron in the pockets of the negative plates. Apparently this oxidation taking place spontaneously is not as easily reduced on succeeding charges as the oxidation which is formed during the normal discharge of the cell. The temporary loss in capacity which results from this effect may require several cycles of charge and discharge to overcome. A battery of the Edison type which has stood idle for two months should receive the following treatment in order to restore it to the former capacity. Discharge it at normal rate through a suitable resistance to as low voltage as possible, preferably zero. Then short circuit it for at least 5 hours. Charge again at the normal rate for not less than 15 hours and discharge at the normal rate again to as low a voltage as possible without short circuiting. Follow this by a charge at the normal rate for not less than 12 hours following which the battery is ready for service.

4. PLATE CAPACITIES

In addition to determining the capacity of storage cells, it is sometimes necessary to determine the capacity of the positive and negative plates separately, as a means of locating faults in the operation of the cells. The capacity of the cells of both the acid and Edison types is normally limited by the capacity of the positive plates. When the capacity of one or more cells in a battery is found to be below normal, and the cause cannot be attributed to internal short circuits or to faulty insulation, the cause of the trouble may often be found in the condition of the active materials. One or the other of the plate groups may be only partially charged, although the battery as a whole is supposed to be fully charged. Inequalities may occur as a result of change in the size of the plates, the loss of active material, or the action of certain impurities. In some lead batteries of poor manufacture, the active material may separate from the grid with the inevitable result that a layer of sulphate forms between the grid and the active material. This layer of sulphate is non-conducting and the active material is prevented from receiving the charging current. The nickel-iron bat-

teries also occasionally show inequalities in the plate capacities which may be due to periods of inactivity or to the materials.

The capacity of the positive and negative plates may be determined separately by the use of a constant auxiliary electrode immersed in the electrolyte of the cell. It is necessary that this electrode should maintain a constant potential with respect to the solution, so that the changes taking place in the positive and negative plates may be measured by the potential differences against this electrode.

a. Auxiliary Electrodes.

A number of different electrodes have been proposed, but the one most generally used for the lead-acid batteries has been the cadmium electrode. The hydrogen and the mercurous-sulphate electrodes are the most accurate for laboratory purposes, but they are not well adapted to ordinary testing. The cadmium electrode is convenient and, if properly used, sufficiently exact for ordinary purposes.

The Hydrogen Electrode.—This gas electrode consists of hydrogen gas absorbed in a layer of platinum black, which may be deposited on one of the noble metals, such as gold or platinum. When the electrode is immersed in a solution containing hydrogen ions, a difference of potential exists between the solution and the electrode. This difference depends on the concentration of the hydrogen ions in the solution. To maintain this potential difference constant at a standard value, the electrode is partly dipped in a solution having a known concentration of the hydrogen ions, such as a normal or a tenth-normal solution, and a stream of purified hydrogen is passed over its upper surface continuously. We cannot measure directly the difference of potential that exists between the electrode and the solution, but we can easily measure the difference in potential between the hydrogen electrode and another electrode with which it is in electrolytic contact. As the basis for an arbitrary scale, the potential of the electrode in a solution that is normal with respect to the hydrogen ions, is sometimes assumed to be zero. With such an electrode as a standard, it is possible to measure the progressive changes that take place in the potential of the plates of an acid storage battery. For the details of the hydrogen electrode and its use, reference should be made to Chapters VIII to XVII of Clark's " Determination of Hydrogen Ions " (1920).

This electrode is adapted to use with the lead-acid batteries, because the solution which is used in it may be sulphuric acid and it cannot contaminate the battery electrolyte in any way. The instrument is delicate and requires a potentiometer for measuring the voltage and a

hydrogen generator to supply the stream of hydrogen gas. It is, therefore, not readily portable.

The Mercurous Sulphate Half-cell.—This electrode is also suitable for use with the lead-acid storage batteries. The cell consists of pure mercury covered with a layer of pure mercurous sulphate and a solution of 1.250 sp. gr. sulphuric acid. This electrode, like the former, is intended for laboratory use only. The constancy of this electrode may be judged from the fact that it is similar to the positive limb of a standard cell.

The Calomel Electrode.—In appearance and structure, this electrode is very similar to the mercurous-sulphate electrode, but as the solution which it contains is potassium chloride it is adapted for use with the nickel-iron storage batteries. It consists of a layer of pure mercury covered with mercurous chloride, commonly called " calomel," and the solution of potassium chloride of a definite concentration. In using either of these electrodes, the end of the glass tube of the electrode is dipped into the electrolyte of the battery.

The Cadmium Electrode.—Cadmium is a metal resembling zinc. It is usually obtained in sticks about $\frac{5}{16}$ inch in diameter, which is a convenient shape for the electrode. Pieces from one to several inches in length are used. The electrodes are prepared for service by keeping them immersed in sulphuric acid solution of about the strength used in the batteries. It is necessary that new electrodes should be in the acid for several days before being used to measure plate potentials. The sulphuric acid corrodes the surface of the electrode, and an equilibrium state is eventually reached.

The cadmium must be insulated so that it cannot come in contact with the plates of the cell, but at the same time the electrolyte of the cell must have free access to the cadmium. A perforated rubber separator from a storage cell is suitable for making the necessary cover for the electrode. A flexible wire for connection is attached to the cadmium. Readings are taken when the current of the battery is flowing, usually on discharge, but sometimes on charge also. The readings are meaningless if the cell is on open circuit. It is sometimes difficult to obtain accurate cadmium readings on exide-ironclad cells because of the interference of the rubber strips on the tops of the plates.

The cadmium electrode is reproducible to about 0.02 volt if precautions are taken. It will remain constant during several hours to within 0.01 volt, but may vary from day to day by 0.02 volt. Amalgamation of the electrode, which is often recommended, does not improve its reliability.[14] In case the electrode surface becomes dry, it must be

[14] The Cadmium Electrode for Storage Battery Testing, by H. D. Holler and J. M. Braham, Bureau of Standards, Technologic Paper No. 146, 1919.

soaked in the acid for at least one-half hour before being used again. The electrode should be immersed as far as possible in the electrolyte in order that as much as possible of the cadmium surface may be used, to avoid polarization.

The greatest error in the use of the cadmium electrode, as found by Holler and Braham, is due to polarization. The ordinary voltmeter of low voltage range has from 100 to 300 ohms resistance. When such an instrument is used it permits sufficient current to flow to partly polarize the cadmium electrode. The error thus introduced may amount to 0.1 volt, which would lead to false conclusions about the condition of the negative plates. The polarization of the electrode is proportional to the potential being measured. It is, therefore, many times greater in measuring the potential of the positive plates than the negative plates, because the potential difference of the electrode and the positive plates is about 2 volts, while the difference between the electrode and the negative plates is only one-tenth as great. The error may be avoided entirely by measuring the voltage on a potentiometer or a high-resistance voltmeter. Such voltmeters may be obtained with a resistance of 25,000 ohms for a full-scale reading of 2.50 volts. In the absence of such means for measuring the voltage, the best procedure is to measure the potential of the negative plates, and from this and the cell voltage calculate the potential of the positive plates. This is easily done, since the potential of the positive plates is the algebraic sum of the cell voltage and the potential of the negative plates. Metallic impurities in the electrolyte, if they are electropositive to cadmium, may lead to false indications of the cadmium electrode. Copper, which is often found in small amounts in storage-battery electrolyte, is an example of this class of impurities. The copper will deposit on the cadmium when it is put into the electrolyte and alter its potential. Reliable readings of the plate potentials can only be obtained with care, and it is essential that the conditions of the experiment be understood to avoid drawing false conclusions in some cases. Typical curves, showing the relation of the cadmium electrode to the potential of the plates, are given in the next section. Zinc is sometimes used in place of cadmium. It is not recommended for lead-acid batteries but may be used in the alkaline type.

b. Plate Potentials During Discharge and Charge.

Lead-acid Cells.—The voltage of the cell is dependent on the potentials of the positive and negative plates with respect to the solution. Since these potentials may vary independently, there are a number of possible combinations of plate potentials that will give any particular

cell voltage. For example, if a group of three cells is measured with a cadmium electrode when each cell has reached its cut-off voltage of 1.8 volts, the following values may be found:

Cell 1, Positive plate, 2.10 Negative plate, 0.30	Cell voltage.....	1.80
Cell 2, Positive plate, 2.00 Negative plate, 0.20	Cell voltage.....	1.80
Cell 3, Positive plate, 1.95 Negative plate, 0.15	Cell voltage.....	1.80

These results require interpretation in the light of the cell's rated capacity and normal performance. The values of the potentials vary with the rate of the discharge, the concentration of the electrolyte, and to a less extent with other factors also. It must be assumed that the voltage drop within the cell, which is equal to the product of the current and the resistance, IR, is negligible. If I is not too large this will be the case, since R is small.

Considering the example given above, the plate potentials of Cell 1 show that the negative plate has reached the limit of its capacity before the positive plate is fully discharged, or in other words, the discharge has been terminated by the negative plate, which is not normal. The positive plate ordinarily limits the capacity of the cell; therefore, in considering the values for Cell 3, it is necessary to know whether the cell gave its rated capacity before reaching the final voltage 1.80. If it did not, the potential readings indicate the positive plates to be deficient in capacity. Although the plate potentials near the end of the discharge are the most important, it is desirable to take the readings throughout the discharge at frequent intervals and from them to plot curves. The values for Cell 2 are about normal for a cell in good condition.

Figure 67 shows in a graphical way the relation of plate potentials of a cell of the lead-acid type designed for service on an electric vehicle, discharging at its normal rate of 45 amperes. The curves show that the capacity of the negatives exceeds that of the positives. It also shows that very satisfactory agreement may be obtained between measurements of the plate potentials obtained by the hydrogen electrode, the mercurous sulphate half-cell, and the cadmium electrode. In order to superpose the determinations of these three electrodes, it has been necessary to displace the zero reference line for each by an amount equal to the difference in potential of the several electrodes. When this is done, the observed values fall on the same curves with a high degree of accuracy.

When lead cells are charged, the relations of the plate potentials are somewhat different. In particular, the potential of the negative plate reverses toward the end of charge, the lead sponge becoming negative with respect to the cadmium by about 0.15 volt. When this occurs the voltage of the cell becomes greater than the potential of the positive plate. At the end of charge, the plate potentials are about as follows:

Positive plate, 2.45
Negative plate, 0.15
} Cell voltage..... 2.60

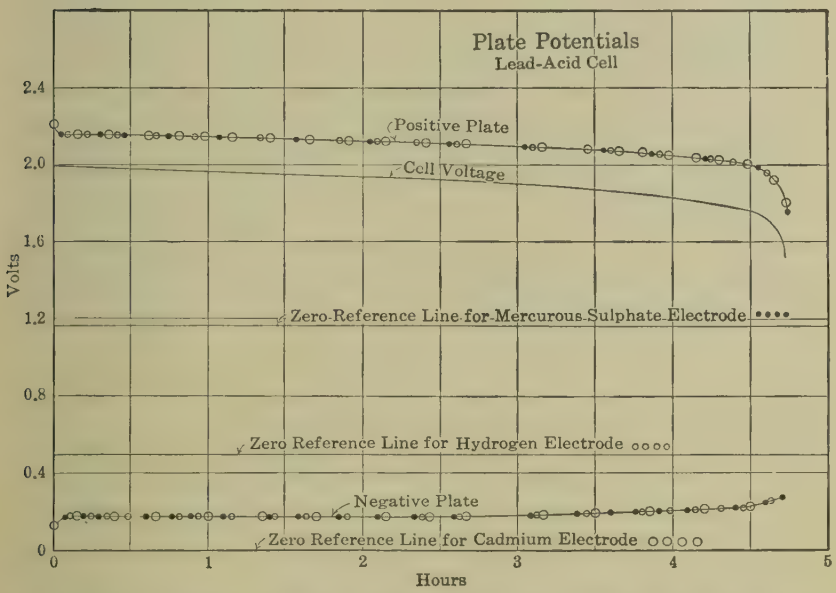


FIG. 67.—Comparison of three auxiliary electrodes for measuring potentials of the plates.

In old cells it is sometimes difficult to make the potential of the negative plate reverse, because of incomplete reduction, which accounts for the lower charging voltages of old cells.

Edison Cells.—The capacities of the positive and negative plates of the nickel-iron batteries may be determined by the use of auxiliary electrodes, in much the same manner as has been described for the lead-acid batteries. If there is an actual falling off in capacity, it is desirable to determine the weak electrode as a first step in seeking the cause of the trouble. Suitable electrodes are the calomel half-cell, for use in the laboratory, or a section of a positive tube taken from an alkaline battery. Connection to this electrode should be made by the

same kind of metal as used for the support of the active material, or else the tube should be made long enough to project out of the liquid. The electrode must be insulated so that it cannot touch the plates. For this purpose a perforated rubber sheet is suitable.

Since it was shown, in the section on the theory of the alkaline batteries, that the positives suffer a spontaneous decomposition of the nickel peroxide to a lower state of oxidation after the charge is completed, it is necessary to partially discharge the intermediate electrode (tube) after charging it, in order to bring it to a stable state. In addition to this precaution, it is also desirable to season the electrode by allowing it to stand in the battery electrolyte for a day or two before use.

The decrease in voltage of the Edison cell during discharge is caused almost entirely by the fall of potential of the positive plate, if the cell is in normal condition. The potential of the iron plate falls slightly at the beginning of discharge to a value which remains practically constant throughout the remainder of the discharge. If the active material of the negative plate is sluggish, however, the negative plate may limit the capacity of the battery, as may easily be determined by single potential measurements.

CHAPTER VI

OPERATION

1. METHODS OF CHARGING

Direct current alone can be used for charging. If alternating current only is available, it must be converted into direct current. This can be done by means of: (*a*) synchronous converter, (*b*) motor generator, and (*c*) rectifier.

There are two systems of charging in general use: (*a*) constant current, and (*b*) constant potential or constant voltage. This latter method is usually modified slightly by the addition of a fixed resistance of small value in series with the battery in order to limit the starting, or inrush, current. Such a system is called a semi, or modified, constant-potential system.

a. Constant Current.

In the constant-current system, as the name implies, the current is held constant by means of a rheostat in series with the battery or by otherwise controlling the voltage of the source.

The current is maintained constant at the normal rate by adjusting the rheostat, cutting out or decreasing the resistance as the charge progresses. This increases the voltage impressed on the battery. The value of the current flowing through the battery is dependent upon the difference between its voltage and that of the charging system.

Let the voltage of the charging system $= E$;
the current flowing at any chosen instant $= I$;
the counter-electromotive force of battery $= E_c$;
the resistance of the battery $= R$.

Then:

$$E = E_c + IR$$

whence

$$I = \frac{E - E_c}{R}$$

Therefore, when the voltage of the battery and the charging system

are the same, no current will flow; when the voltage of the battery is lower than that of the charging system, current will flow into the battery and charge it; and when the voltage of the battery is higher than that of the charging system, current will flow out of the battery and discharge it. As the voltage of the battery increases gradually with the progress of the charge, it is apparent that the voltage impressed across its terminals must be increased in order to maintain a constant value for the charging current. For batteries of the lead-acid type, the specified current is maintained until all cells are gassing freely and then reduced to a much lower value designated as the finishing rate, at which the charge is continued to the end. The value of the finishing

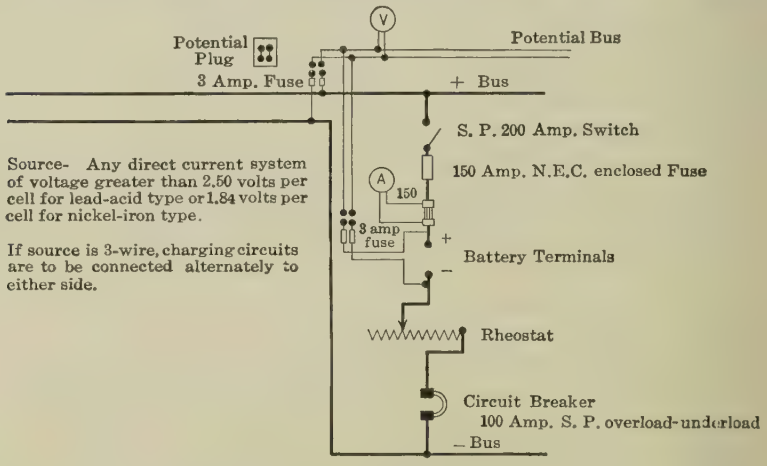

V
Potential Plug
Potential Bus
3 Amp. Fuse
+ Bus
S. P. 200 Amp. Switch
Source- Any direct current system of voltage greater than 2.50 volts per cell for lead-acid type or 1.84 volts per cell for nickel-iron type.
If source is 3-wire, charging circuits are to be connected alternately to either side.
A
150
150 Amp. N.E.C. enclosed Fuse
3 amp fuse
+
Battery Terminals
–
Rheostat
Circuit Breaker
100 Amp. S. P. overload-underload
– Bus

FIG. 68.—Battery charging circuit, constant current method. *A*, ammeter; *V*, voltmeter.

rate is approximately 40 per cent of the starting rate. The ampere-hours required to produce free gassing of a lead battery at the normal starting rate of charge will be approximately 90 per cent of the ampere-hours previously discharged. At this point the current should be cut down to the finishing rate and the charge continued until the battery begins to gas freely again.

Figure 68 is a diagram of connections for a typical constant-current charging circuit.

In order to obtain most efficient results with batteries of the lead-acid type, the voltage of the charging circuit should be approximately 2.5 volts per cell at normal temperatures with current flowing at one-half the value of the finishing rate. When the voltage of the circuit exceeds this value, the maximum resistance of the rheostat must be

sufficient to permit of a reduction in voltage to this value. It is desirable that the ampere capacity be sufficient to permit a current value of four or five times the normal, to permit of boosting (see p. 225) provided that the wiring of the charging circuit can safely carry that current. In a new installation, this condition can be provided for readily. In modifying an existing installation, the current capacity of the rheostat need not exceed the safe current-carrying capacity of the circuit.

The value in ohms of the resistance equals

$$\frac{A-(B\times C)}{D}$$

in which A = voltage of system;

B = number of cells in battery;

C = volts per cell, a constant, 2.5 for all types and sizes of lead-acid cells; for nickel-iron types $C=1.7$ volts per cell;

D = 50 per cent of finishing rate in amperes.

Example.— Assume a 17-plate battery of 24 cells having a normal charging rate of 45 amperes and a finishing rate of 18 amperes; charging circuit 110 volts—

Resistance in ohms equals

$$\frac{110-(24\times 2.5)}{9}=5.6$$

The current capacity equals

$$5\times 45=225 \text{ amperes.}$$

Such a rheostat, unless properly designed, would be large and expensive. The excessive capacity may be reduced by designing the variable portion so that at each step the current-carrying capacity is just within the safe limit. A simpler arrangement, which would provide for the boosting current and also permit of sufficiently good regulation for charging under ordinary conditions, could be made as follows: Ten fixed resistances, each connected as required between the bus and the battery by a single-pole switch, are arranged so that the first three switches would connect in 6 ohms each; the next three, 3 ohms each; and the seventh to the tenth switches, 1.5 ohms each. This rheostat would provide, under the conditions given in the example, a maximum current of 210 amperes, and a minimum current of 8.3 amperes. The maximum kilowatt capacity when all resistances are in parallel would be 10.6 kilowatts, and the minimum capacity 0.4 kilowatt for the smallest charging current.

For batteries of the nickel-iron type, charging at constant current is carried on at the normal rate for the full period of time required, normally 7 hours, or until the voltage becomes constant, at least 1.85 volts per cell. As the specific gravity of the electrolyte of batteries of this type remains constant during charge or discharge, the only indications of complete charge are the condition of voltage as stated above and the length of time taken for the charge. If the battery shows a temperature exceeding 46° C. (115° F.) it should be cut off immediately from charge and allowed to cool.

b. Constant Potential.

In the constant-potential, or constant-voltage method, the voltage is maintained at a constant fixed value per cell. The value of the initial, or starting, current of a completely discharged battery when first put on charge is much in excess of that of the normal rate. During the charge, as the voltage of the battery gradually rises, the current falls off to a value much below that of the normal rate, and at the end of the charge is below that of the finishing rate of the constant-current system. The average value of the current is about equal to that of the normal rate.

For batteries of the lead-acid type, the maximum voltage should not exceed 2.4 volts per cell, and the minimum should not be less than 2.2 volts per cell. The average should be approximately 2.3 volts per cell. It is to be noted that these values of voltage are those at the terminals of the battery. In practice, when using the modified constant-potential method, the voltage at the bus may range from 2.45 volts to 2.90 volts per cell.

With the average voltage thus established at approximately 2.3 volts per cell, a battery in any state of discharge may be put on charge and it will automatically receive the proper charge without reaching the free gassing point or excessive temperature.

The time required for a completely discharged battery to receive a 100 per cent charge—the number of ampere-hours taken out on the previous discharge—will be approximately 3 hours, or 60 per cent of the time of normal discharge.

It sometimes happens that the charging unit or generator is of relatively small capacity. In such a case it is necessary to limit the initial, or starting, current and to accomplish this a fixed resistance of small value is placed in series with the battery. This is known as a semi-constant-potential or a modified constant-potential system. Figure 69 is a diagram of connections for such a system with a three-

wire supply. For a two-wire supply the connections are the same as shown on this diagram for circuit B, or between the two outside wires.

Figure 70 [1] is a series of curves from which the value of fixed resistance and the initial current of a modified constant-potential charging system may be obtained.

The horizontal scale shows the "bus voltage per cell"; that is, the total voltage of the charging system divided by the number of cells in the battery. The vertical scale for the lower set of curves shows values of resistance in ohms per cell which, when multiplied by the

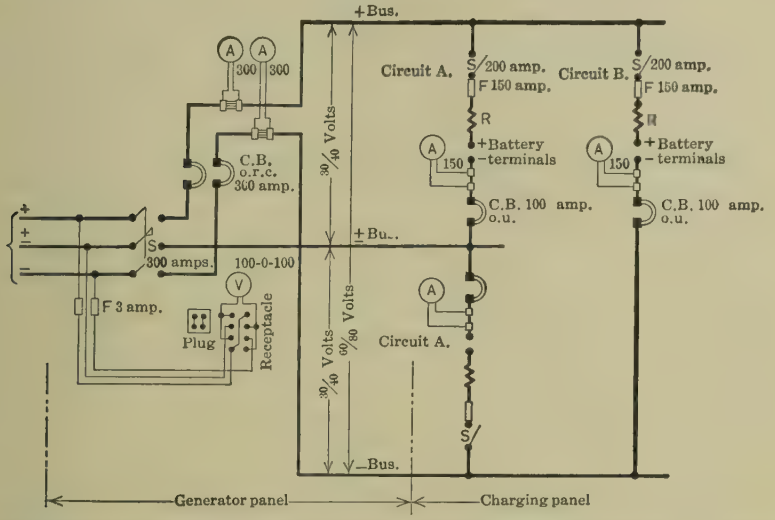


FIG. 69.—Battery charging circuit, modified constant potential method. *A*, ammeter; *V*, voltmeter.

number of cells in the battery, gives the value of the fixed resistance to be used in the charging circuit. The vertical scale for the upper set of curves shows the initial value of the charging current. The line *A* shows the condition of bus voltage and resistance for batteries to finish the charge at the finishing rate; similarly line *B* is for one-half the finishing rate, and line *C* at 125 per cent of the finishing rate. It is desirable to finish between lines *A* and *B*.

It is to be understood that the values of initial current and time for a complete charge obtained from these data are not absolutely fixed,

[1] For a complete discussion of the constant-potential method of charging, reference is made to Bulletin No. 189 of the Electric Storage Battery Co., Charging Equipment for "Ironclad-Exide" and "Exide" Storage Batteries in Locomotives, Trucks and Tractors, from which part of this discussion has been taken.

but are subject to variations due to temperature, age of cells, time standing idle after discharge, etc.

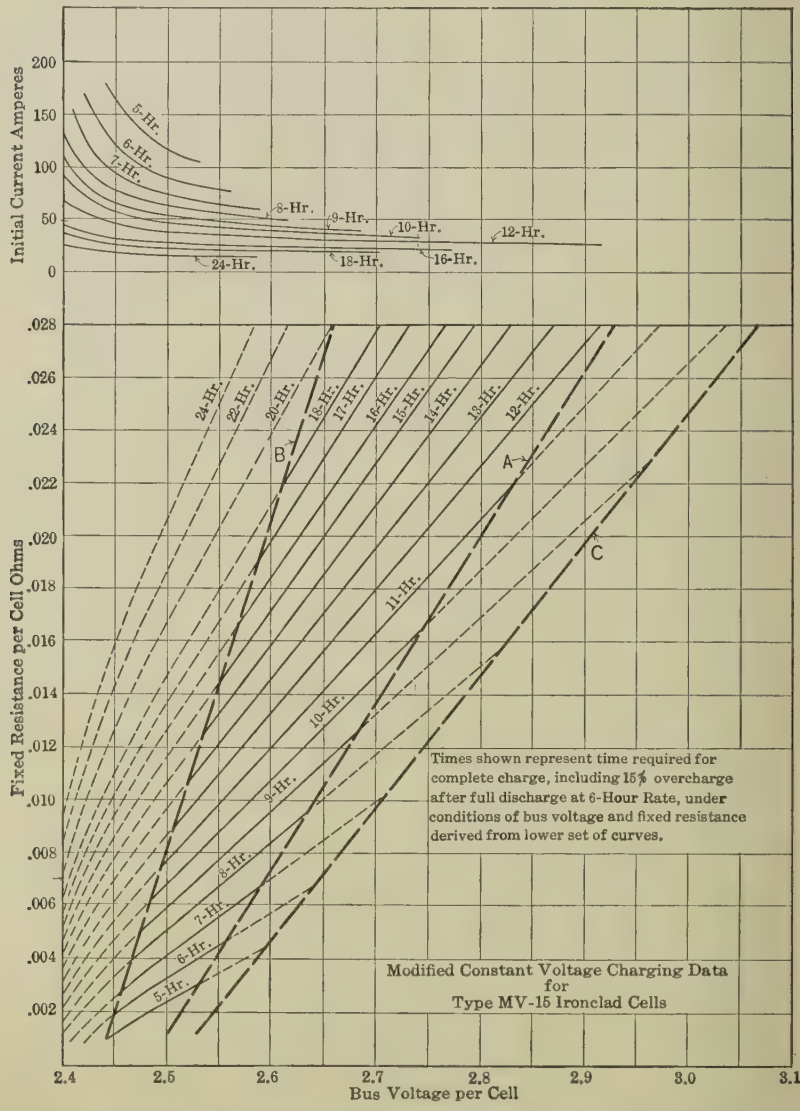


FIG. 70.—Relation of fixed resistance to time and initial current, modified constant potential charging.

The curves apply to a cell of 15 plates with a capacity of 238 ampere-hours at the 6-hour rate of discharge. In order to make them applicable

to other cells, corrections must be made based on the capacity at the corresponding rate of discharge. Thus, for a cell of 13 plates with a capacity of 147 ampere-hours at this rate, $\frac{147}{238}=0.62$, a constant by which the value of current read from the curve must be multiplied in order to obtain the correct value for this type of cell. The value of resistance read from the curve must be divided by this constant and multiplied by the number of cells in the battery in order to obtain the correct value. Assume a battery of 12 cells each having 13 plates, and a capacity of 147 ampere-hours, a bus voltage of 2.5 volts per cell and 6 hours available time for charging. The initial current as taken from the 6-hour curve of the upper set corresponding to 2.5 volts per cell is 91 amperes which, multiplied by the constant $0.62=56.5$ amperes, the correct initial current which must be provided for in the charging circuit. The resistance, as taken from the corresponding curve of the lower set, is 0.0033 ohm which, divided by the constant 0.62 and multiplied by 12, the number of cells, $=0.064$ ohm, the value of the fixed resistance to be used in the charging circuit. A resistor having a resistance of 0.07 ohm and a current-carrying capacity of 60 amperes will be required. In order to provide for variation in results due to temperature, etc., it is well to provide taps on the resistor.

The resistor should always have a carrying capacity in amperes not less than the initial current. As such resistors ordinarily have very little overload capacity, a factor of safety should be used which will provide a margin to meet any unusually severe condition which may arise. Switches, circuit breakers, and wires have some overload capacity, but in order to comply with the Underwriters' requirements, the continuous rating should be equal to the initial current.

When it is desired to make the charging system automatic, an ampere-hour meter affords the most reliable means for terminating the charge. In this connection the circuit breaker must be provided with a shunt trip attachment having auxiliary contacts to open the tripping circuit and thus avoid arcing at the contact of the ampere-hour meter (see p. 249). The meter is to be provided with a zero contact, a resetting device, and a fixed red hand set at the discharge limit. It should be adjusted to run slower on charge than on discharge. The meter must be connected in the battery circuit during discharge as well as during charge.

For any battery, the higher the bus voltage the greater will be the loss in the resistance, with a decrease in efficiency and an increase in the length of time required for the charge. On the other hand, if the bus voltage is but a little higher than that of the battery, the charging

current will become more or less unstable and subject to considerable variation with changes in temperature of the battery and slight changes in the bus voltage.

When the time available for charging is limited, or efficiency is of considerable importance, a bus voltage of approximately 2.6 volts per cell is found to be generally satisfactory.

As the bus voltage and resistance are increased for the same number of cells in the battery, the charging current becomes more nearly constant throughout the charge, thus approaching the constant-current method.

For the constant-potential method, the voltage at the charging panel should be that delivered by the generator or other source of energy. If this is not so, counter cells may be used to reduce the voltage at the terminals of the battery to the proper value. A resistance of sufficient value, in series with the battery, to reduce the voltage will not produce the desired results. In such a case it is preferable to use the constant-current system.

For batteries of the nickel-iron type, the impressed voltage should not be less than 1.70 volts per cell. As in the case of the lead-acid type, the voltage at the charging panel must be slightly higher than this value. In practice this will be about 2 volts per cell. When batteries of this type are to be charged from a semi-constant-potential system, the resistance R is given in Table XLI.

TABLE XLI

MODIFIED CONSTANT-POTENTIAL CHARGING OF EDISON BATTERIES

The fixed resistance to be placed in series with the battery is calculated on the basis of the resistance required in a 110-volt circuit to charge a 60-cell battery. Constant potential 1.84 volts across cell and its fixed resistance, average voltage at cell terminals, 1.686 volts.

Type of Cell	Normal Charging Rate	Fixed Resistance per Cell, Ohms
A 3	22.5	0.0067
A 4	30.0	0.0050
A 5	37.5	0.0040
A 6	45.0	0.0033
A 7	52.5	0.0029
A 8	60.0	0.0025
A 10	75.0	0.0020
A 12	90.0	0.0017

c. Equalizing Charge.

Once a week, a lead battery such as is used for operating a truck or tractor should be given an overcharge known as an "equalizing charge." For this the charge is to be continued from the normal end at a rate equal to approximately one-half the value of the finishing rate until all cells are gassing freely and uniformly, and until three consecutive readings of the specific gravity and voltage taken at half-hour intervals show no increase. If a battery shows a temperature exceeding 43° C. (110° F.) it should be cut off immediately and allowed to cool.

Once a month, the voltage and gravity readings of each cell should be recorded. These will serve as an indication of trouble within the cells, such as sulphation or leakage, if there is a progressive change of the gravity readings.

The gravity of the individual cells should be adjusted to the proper value when the battery is first put in service or when it has been necessary to add electrolyte to any cell to replace electrolyte which has been spilled or otherwise lost. This should be done at the end of the equalizing charge. If the gravity of the cell is too high, a portion of the electrolyte may be withdrawn with the hydrometer syringe and replaced by distilled water. Similarly, the gravity may be increased by replacing the portion drawn off by electrolyte of not over 1.400 sp. gr. Before the adjustment is considered complete, the equalizing charge should be continued to mix the electrolyte of the cell. The final value is shown by several consecutive constant readings at 15-minute intervals. The gravity should be adjusted to within 5 points, corrected for temperature, of the proper value. Alkaline batteries occasionally require an equalizing charge of 12 hours at the full charging rate. When the specific gravity of the electrolyte for these has fallen to the limits set in Chapter III the electrolyte should be renewed.

d. Boosting.

Under certain conditions, the ampere-hour capacity of the battery may be insufficient for the day's work. In such a case, charging at a high rate of current for a short time may be resorted to. Such a charge is known as "boosting" and is usually given the battery during the noon hour.

Figure 71 shows the value of current, with time, to be used for boosting, for the lead-acid type. Batteries of the nickel-iron type may be boosted, provided the temperature of the inside cells does not

exceed 46° C. (115° F.). The rates of charge for cells of the A type, recommended by the Edison Storage Battery Co., are as follows:

5 minutes at 5 times normal rate.
15 minutes at 4 times normal rate.
30 minutes at 3 times normal rate.
60 minutes at 2 times normal rate.

Frothing at the filler opening is an indication that the boosting has been carried too far.

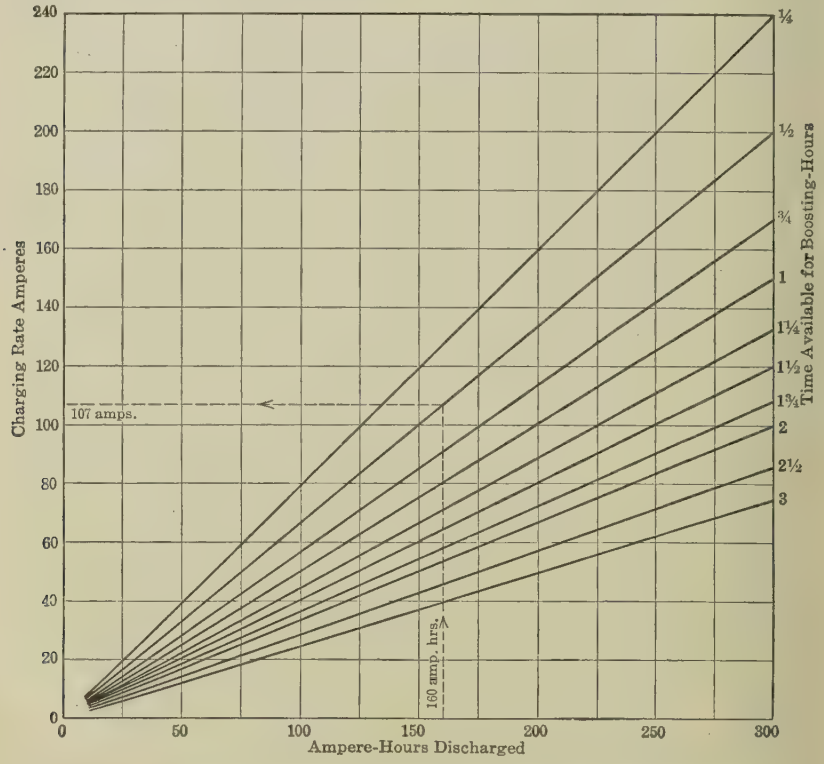


Fig. 71.—Maximum rates for boosting lead-acid cells of any capacity.

Example: If 160 ampere-hours have been discharged and one-half hour is available for boosting, follow the dash lines in the direction of the arrows. The proper value of the current to use is found to be 107 amperes.

With the constant-current system, the rheostat is adjusted in order to maintain the current at the constant value. When charging is to be done by the constant-potential method in a given number of hours, reference should be made to Fig. 70 or Table XLI.

e. Trickle Charge.

By trickle charging is meant the charging of a battery at a very low rate over a long period of time. The trickle charge may be adjusted to replace the current drawn from the battery periodically, plus the loss arising from local action; or, if the batteries are not in use, it may be merely sufficient to counteract the local action. Low-rate charges are satisfactory for lead batteries provided the total amount of charge received by the battery is sufficient to cover the discharge of use and local action. This method of charging is particularly satisfactory for plates of the pasted type. Several applications have been made of trickle charging. One of them is to put batteries in so-called " wet " storage. This applies to vehicle batteries and batteries for starting and lighting of automobiles which are to remain out of use for several months or more. In order to maintain these batteries in good condition, they may be kept on continual charge at a low or trickle rate. The amount of current required is just enough to offset the local action and to keep the specific gravity within the cell constant. The actual value of the current will depend upon the concentration of the electrolyte and the temperature, as these factors affect the rate of local action; but this is approximately equal to $\frac{1}{2}$ to 2 per cent of the 8-hour discharge rate. A number of cells of the same capacity may be charged in series, and the regulating resistance in the circuit may conveniently be a bank of incandescent lamps. These provide an inexpensive method of adjusting the charging current as shown in Table XLII and at the same time provide an indication that the batteries are on charge. At regular intervals, the filling plugs should be removed and water added to the cells if necessary. At the beginning of the charge the specific gravity of each cell should be read and recorded, and this operation should be repeated at intervals. The charging current may then be reduced to the lowest limit which will keep the specific gravity constant.

Another application of trickle charging is to the batteries which operate railway signals. These batteries are required, from time to time, to deliver currents of several amperes, for the operation of semaphores and track switches. During a large part of the time the batteries are idle, and it is possible to keep them fully charged by the use of small rectifiers connected to an alternating-current power line. The charging current from these rectifiers is continuous but small. A third type of trickle charging is found in the use of small rectifiers of the vibrating-reed or bulb type with radio batteries. These batteries are required to have considerable ampere-hour capacity for the operation of vacuum tubes, but may be charged at a low rate over considerable periods of

time when not in use. Trickle charging is not recommended for batteries of the alkaline type. These batteries, if charged at rates below normal, do not give their full capacity on subsequent discharge.

TABLE XLII

Combinations of Tungsten Lamps Required for Trickle Charging of Lead-acid Batteries

(Lamps rated for 110 volts. Combinations to be used in series with the batteries across a bus of 105 to 115 volts.)

Number of Cells	For 0.05 Ampere	For 0.10 Ampere	For 0.15 Ampere
3	Five 15 W. lamps in series	Three 25 W. lamps in series	Two 25 W. lamps in series
30	Two 15 W. lamps in series	One 25 W. lamp	
45	One 15 W. lamp	Two 25 W. lamps in parallel	Three 25 W. lamps in parallel

f. The Conditions for Floating.

A battery is said to float upon a charging line when the voltage of the charging line is slightly greater than the open-circuit voltage of the battery, and opposite in polarity. For the ordinary type of lead cell, the voltage at which the cell will float is about $2\frac{1}{10}$ volts, but there is a range of approximately .1 volt from 2.05 to 2.15 volts, between which the charging or discharging current from the battery is extremely small. When a floating battery is connected to a line of which the voltage is approximately equal to the open-circuit voltage of the battery, the battery will charge or discharge according as the fluctuations of current of the line rise above or fall below the voltage at which the battery floats.

A battery which is properly floated upon a power line will automatically take care of the power required for a fluctuating load, and the battery will be maintained in the fully charged condition. Railway signal batteries, mentioned in the section on trickle charging, illustrate one form of the floating battery. The voltage provided by the rectifiers is approximately 2.15 volts, which is only slightly above the floating voltage. By maintaining the voltage at this figure, the battery is on charge at a very low rate, but when required to furnish power

for the operation of signals or track switches the battery discharges through a circuit in parallel with the charging circuit. The so-called line batteries of large capacity, which may be located at points remote from the generating equipment, as in the case of electric railways, are another form of floating battery. It is not necessary, however, that the battery should be at a point remote from the generator. It may be connected directly across the terminals of the generator, if of the under-compound type. A third type of floating battery is found on submarines, where the battery may be used as a brake on the marine engines to prevent them from racing in heavy seaway. To accomplish this successfully, the battery must be in a partly discharged condition in order to provide a sufficient load on the generator. The battery is adjusted to float on the line when the generator is running at its normal speed. If the engine driving the generator tends to race because of the propellers emerging from the water, the increased voltage of the generator at once starts a heavy charge through the battery, with the result that the battery acts as a brake on the engine. Edison batteries can not be as successfully floated on a line as the lead type, because they have a voltage characteristic that is steeper.

2. CHARGING AND DISCHARGING LEAD BATTERIES

a. Discharge.

Voltage Characteristics.—When a storage battery of the lead type begins to discharge, there is an initial drop in voltage, which may be attributed in part to the ohmic resistance of the battery and in part to the sudden decrease in concentration of the acid in the pores of the plates, which reduces the potential of the plates. This abrupt drop in voltage is often followed by an almost equally abrupt rise in voltage. Such an effect may be seen at the beginning of the discharge curve in Fig. 72. No designation in English has been applied to this peculiar phenomenon, butin French it is referred to as the *coup de fouet* (stroke of a whip). This effect has been ascribed to various causes and it is not always present. After the sudden decrease in concentration of the acid when discharge begins, the diffusion process is started and the stronger acid from outside the plates, diffusing into the pores of the plates, tends to restore the voltage.

In addition to this effect, there may also be a gradual rise in voltage during the early stages of discharge, particularly if the battery has stood for some days since being charged. This is attributed in part to the decreased resistance of electrolyte as the temperature is raised and also to the decrease in concentration within the range 1.300 down

to 1.225, for which the resistivity is a minimum. During the greater part of the discharge, the voltage falls slowly from a value approximately equal to the open-circuit voltage to about 1.8 volts. The decrease in voltage is caused by a decrease in the plate potentials, as the rate of diffusion of the electrolyte fails to keep pace with the consumption of acid within the pores of the plates; to a less extent it may be attributed also to the increasing resistivity of the electrolyte as the concentration falls below a specific gravity of 1.225. When near the end of the discharge, the curve shows a more abrupt drop; this point

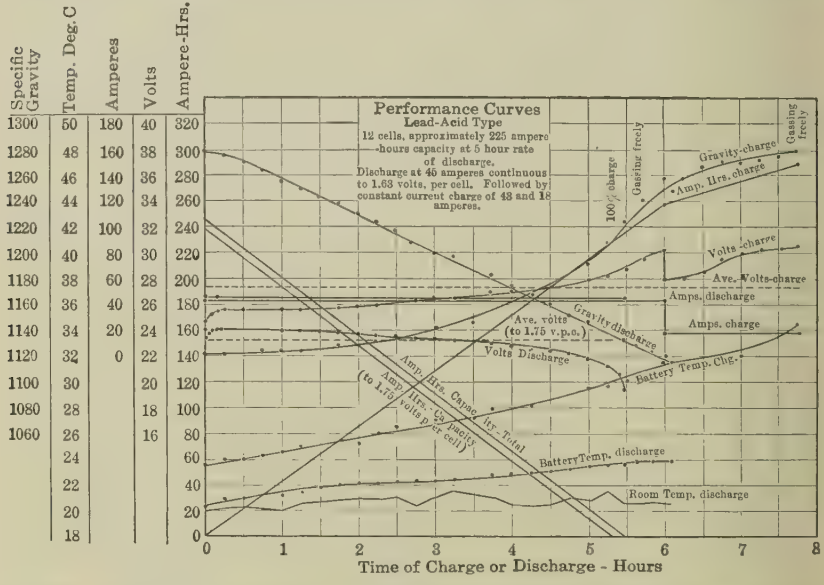

Specific Gravity
Temp. Deg. C
Amperes
Volts
Ampere-Hrs.
1300 1280 1260 1240 1220 1200 1180 1160 1140 1120 1100 1080 1060
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18
180 160 140 120 100 80 60 40 20 0
40 38 36 34 32 30 28 26 24 22 20 18 16
320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0
Performance Curves
Lead-Acid Type
12 cells, approximately 225 ampere-hours capacity at 5 hour rate of discharge.
Discharge at 40 amperes continuous to 1.63 volts, per cell. Followed by constant current charge of 48 and 18 amperes.
100% charge
Gassing freely
Gassing freely
Gravity charge
Amp. Hrs. charge
Volts charge
Ave. Volts charge
Amps. discharge
Amps. charge
Ave. volts (to 1.75 v.p.c.)
Gravity discharge
Volts Discharge
Battery Temp. Chg.
Amp. Hrs. Capac. Inc. Total
Amp. Hrs. Capacity (to 1.75 volts per cell)
BatteryTemp. discharge
Room Temp. discharge
0 1 2 3 4 5 6 7 8
Time of Charge or Discharge - Hours

FIG. 72.—Curves of discharge of a lead-acid battery, followed by charge by the constant current method. Cells were of the vehicle type.

is known as the knee of the curve. It signifies that the complete exhaustion of the cell is approaching. The knee of the curve is less distinct in discharges at high rates than at low rates.

The average voltage during the period of the discharge is the factor which is of importance in determining the amount of energy delivered by the battery. The average voltage is determined from the time integral of the voltage curve from the beginning to the end of discharge. The average voltage varies with the rate at which the discharge takes place, with the type and construction of the cells, and also with the cut-off voltage. Under normal conditions for vehicle batteries of the lead-acid type, the average voltages are approximately as follows:

At $\frac{1}{2}$ the normal rate			1.97	volts	per cell
At 1 times the normal rate			1.95	"	"
" 2	"	"	1.90	"	"
" 3	"	"	1.85	"	"
" 5	"	"	1.75	"	"
" 10	"	"	1.50	"	"

Wide separation of the plates, abundance of electrolyte, and relatively low rates of discharge afford discharge curves with the most nearly flat characteristic.

Temperature.—The temperature of batteries of the lead-acid type rises slowly during discharge, but the effect is much less than is observed when the same batteries are on charge at the same current. The reason for this has been pointed out in Chapter IV, where it was shown that there are two heat effects, one caused by the ohmic resistance and varying as the square of the current, and the other a reversible heat effect varying directly as the current. These two heat effects are opposed during discharge. The one resulting from the ohmic resistance of the cell generally overbalances the second heat effect, so that the temperature of the battery rises. Since the irreversible heat effect varies as the square of the current, the temperature rise will be considerably greater when the rate of discharge is increased.

Specific Gravity.—The specific gravity of the electrolyte falls almost lineally during discharge, provided the discharge current is constant. The specific gravity of the electrolyte, therefore, affords a valuable means of checking the state of charge of the battery. If readings are taken for a time after the discharge has been stopped, it will be observed that there is a continued fall in specific gravity until the concentration of the dilute electrolyte in the pores of the plates has been equalized with the more concentrated acid outside.

b. Charge by Constant-current Method.

Voltage Characteristics.—When a storage battery is first put on charge, a sharp rise in the terminal voltage of the cell is noticed. This is probably to be ascribed to the sudden increase in concentration of the electrolyte as sulphuric acid is liberated in the pores of both the positive and negative plates. The diffusion processes begin and check the rise in voltage. Equilibrium is reached when the rate of diffusion of the concentrated acid from within the pores keeps pace with its formation. There is sometimes a slight drop in voltage after the first few minutes, which gives to the curve a shape somewhat similar to the *coup de fouet*, noticed in connection with the voltage characteristics

on discharge, but in the reverse direction. The cause for this drop is not known with certainty, but has been ascribed to the breaking down of a continuous film of sulphate with consequent decrease in the internal resistance of the cell.

Following this point, the curve representing the terminal voltage of the cell continues to rise gradually to the point which is designated as 100 per cent charge in Fig. 72. By 100 per cent charge is meant a charge equal in ampere-hours to the preceding discharge. In Fig. 72 the 100 per cent point is found at $5\frac{3}{4}$ hours. The increase in the potential at the cell terminals during this period is to be ascribed to the increasing concentration of the acid within the cell. It cannot be accounted for on the ground of internal resistance, since it is well known that the internal resistance of a cell decreases during the charging period.

At the time the 100 per cent charging point is reached, or slightly before, a more abrupt rise in the voltage is noted. This is due only in part to the increasing concentration of the acid within the pores. At this time, most of the sulphate which is readily available for the action of the current has been broken down and the concentration of sulphate in the electrolyte has diminished. A consideration of the Nernst equation, relating the potentials of the plates to the ionic concentrations in the electrolyte, shows that as the number of lead or lead-peroxide ions is diminished the potential of the plate is increased. Therefore, when the lead sulphate on the plates becomes exhausted and the lead-sulphate ions in the electrolyte are diminished, the plate potential will rise to a point at which decomposition of water will take place. This is made evident by the formation of gas, including both oxygen and hydrogen, which escapes freely from the cell during the latter part of the charge. The gassing becomes free, as Fig. 72 indicates, at the end of about six hours. If the charging rate is reduced at this time, the potential of the plates is lowered and the gassing is decreased.

It is common practice in charging a storage battery by the constant-current method, to decrease the charging current to what is called the finishing rate near the end of the charge. The object of this is to avoid the hard gassing which would otherwise take place. The best rule is to reduce the starting charging rate to the finishing rate when the battery has received 90 per cent charge. In Fig. 72 the reduction was made about half an hour after this point was reached.

The voltage at the terminals of the cell begins to rise again after dropping with the reduction in charging rate as shown in Fig. 72. It finally reaches about 2.5 to 2.6 volts per cell, at which time the battery is again gassing freely.

Gassing.—The point at which gassing of a storage battery while on charge, begins is determined by the voltage, but the quantity of gas depends on the current which is not absorbed by the battery. The gases liberated are oxygen, evolved at the positive plates during charge, and hydrogen, evolved at the negative plate. It is not uncommon, however, for one plate to begin gassing before the other, and therefore the gas liberated from a storage cell, in the early stages at least, does not always correspond to the proportions of oxygen and hydrogen which form water. The gassing begins when the voltage at the terminal of the battery has reached about 2.3 volts per cell. The following table, obtained from a test, shows that during the early stages the gas is almost equal parts of oxygen and hydrogen; but as the charge approaches the end, when the cell voltage has risen to 2.5 per cell, the gas has a composition of two parts hydrogen to one of oxygen.

TABLE XLIII

DATA ON GASSING

Per cent by volume)

Cell Voltage Volts	Gassing	Composition	
		Hydrogen, Per Cent	Oxygen, Per Cent
2.20	None	....	....
2.30	Slight	52	47
2.40	Normal	60	38
2.50	Hard	67	33

Since oxygen and hydrogen unite with explosive violence to form water from the gases liberated from a storage battery during charge, it is necessary that certain precautions be taken to avoid accident. Open flames of any kind in a storage-battery room are not permissible, and suitable ventilation should be provided to prevent an accumulation of hydrogen. Four per cent of hydrogen in the atmosphere is dangerous, and the concentration should be kept much below this figure. In the latter part of this chapter is an illustration, Fig. 107, which shows the result of an explosion of the gas in a storage cell.

Storage cells of the lead-acid type do not gas during discharge or when standing idle under ordinary conditions. There is, however, often a slight liberation of hydrogen from the negative plates because

of local action which takes place when the cell is idle. It should always be presumed, therefore, that hydrogen is present within the space over the electrolyte, and precautions, necessary to avoid explosions as when the cell is on charge, should be observed at all times. It is particularly dangerous to use a lighted match over the vent of a cell to see how high the liquid stands.

Specific Gravity.—The changes in specific gravity of the electrolyte during the charging period are shown by a curve in Fig. 72. The most noticeable fact concerning this curve is the very slow rise during the first two hours. After this time the curve rises more rapidly, following in an approximate way the curve representing the ampere-hours of input. Toward the end of the charging period, the curve of specific gravity rises much more slowly, practically following the decrease in charging rate. One may ask why the specific gravity shows such a slow rise during the first few hours, although the fall in specific gravity when the same cell is on discharge is well marked during that period. The reason is that the concentrated acid, as it is liberated from the pores of the plates, falls to the bottom of the cell. The rapid rise when the cell begins to gas freely is caused by the bubbles of gas stirring up the electrolyte. In the case of the discharge, the more dilute electrolyte rises to the top. In a cell made as compactly as the vehicle type, for which the performance curves are shown in Fig. 72, it is not possible for the acid to circulate throughout the cell as rapidly as would be the case in a cell of the stationary type with wider separation between the plates.

Temperature.—Referring again to Fig. 72, the temperature of the battery is seen to rise continuously throughout the period of charging, and it should be noted that the increase in temperature during the charging period is considerably greater than the increase in temperature during the discharge of the same cell at the same rate of current. This is explained by the fact that heat generated because of the internal resistance of the cell and the reversible heat effect, which was discussed in Chapter IV are both in the same direction. The reversible heat effect in this case is exothermic, whereas on discharge it was endothermic.

c. Charge by Constant-potential Method.

Tapering Current.—In addition to charging batteries by the constant-current method, which has been described in the preceding section, it is possible to charge them by the constant-potential, or tapering-current, method. The voltage at the terminals of the cell is held constant at a value of approximately 2.3 volts per cell. The current meanwhile varies from large values at the beginning to small

values at the end. In order to avoid excessive currents, use is commonly made of a small resistance in series with the battery which serves to limit the maximum inrush of current. The method is then known as the modified constant-potential method of charging (see p. 222). The point at which 100 per cent charge is given to the battery comes much earlier with this method than with the constant-current method. Referring to Fig. 73, it will be seen that the 100 per cent charge point is reached at about 3 hours. This means that a much greater percentage of the charge can be given to a battery in a limited time by this method than by the constant-current method. It should not be concluded,

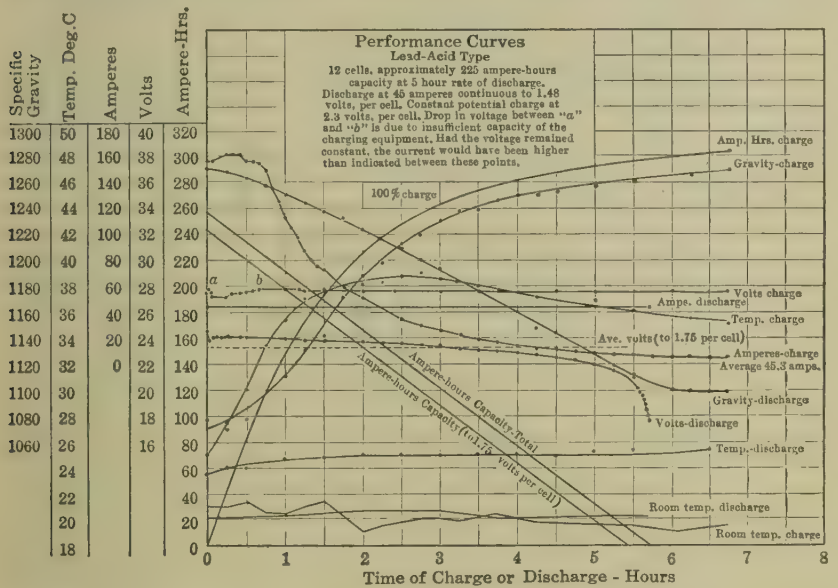

Specific Gravity
Temp. Deg. C
Amperes
Volts
Ampere-Hrs.
Performance Curves
Lead-Acid Type
12 cells, approximately 225 ampere-hours capacity at 5 hour rate of discharge. Discharge at 45 amperes continuous to 1.48 volts, per cell. Constant potential charge at 2.3 volts, per cell. Drop in voltage between "a" and "b" is due to insufficient capacity of the charging equipment. Had the voltage remained constant, the current would have been higher than indicated between these points.
100% charge
Amp. Hrs. charge
Gravity-charge
Volts charge
Amps. discharge
Temp. charge
Ave. volts (to 1.75 per cell)
Amperes-charge
Average 45.3 amps.
Gravity-discharge
Volts-discharge
Temp.-discharge
Ampere-hours Capacity-Total
Ampere-hours Capacity (to 1.75 volts per cell)
Room temp. discharge
Room temp. charge
Time of Charge or Discharge - Hours

FIG. 73.—Curves of discharge of a lead-acid battery, followed by charge by the modified constant potential method.

however, that the time for a complete charge by the constant-potential method is much less than by the constant-current method, because beyond the 100 per cent charge the current tapers off to a small value, so that it requires considerable additional time to give the battery a complete charge unless the charging rate is held to the finishing rate near the end.

Specific Gravity of the Electrolyte.—Figure 73 shows that the specific gravity begins to rise noticeably almost immediately, and after one hour has elapsed the curve representing the increase in specific gravity parallels the curve representing the ampere-hours put into the battery.

Temperature.—The temperature of a storage battery on charge by the constant-potential method rises with great rapidity at the beginning of the charge. This is because of the heat generated within the cell as a result of the current and the internal resistance of the cell, both of which are large during the early stages of the charge. Figure 73 shows that the temperature reached a maximum value at about $2\frac{1}{2}$ hours after the beginning of the charge, and after this time the temperature fell steadily.

d. Comparison of the Constant-current and Constant-potential Methods of Charging.

In Fig. 74, which is taken from an article by Woodbridge,[2] a comparison of the rate of charging by the constant-current and constant-

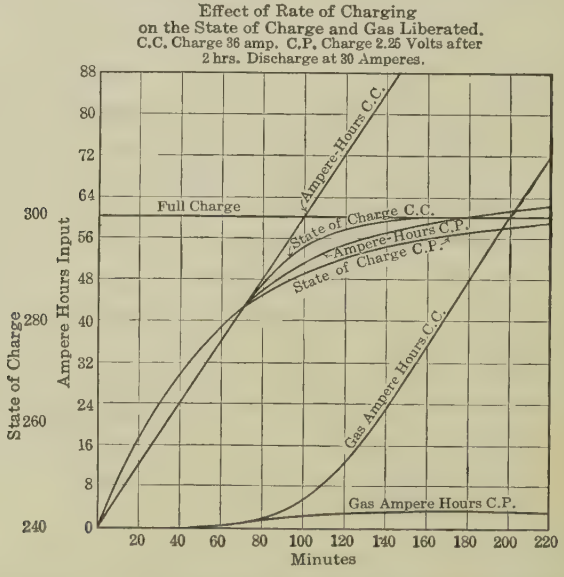


FIG. 74.—Comparison of the constant current and constant potential methods of charging.

potential methods and its relation to the state of charge and the gas liberated is shown. It has been stated above that charging takes place more rapidly by the constant-potential method during the early stages of the charge, and Fig. 74 applies particularly to a comparison of the two methods when the charge is nearly complete. A storage battery of 300 ampere-hour capacity, fully charged, was discharged

[2] Railway Electrical Engineer, Vol. 9, p. 6, 1918.

to the extent of 60 ampere-hours and then put on charge by the constant-current and constant-potential methods successively. The curves show that the rate of charging by the constant-potential method is slightly greater than by the constant-current method, but that the curve representing the state of charge by the constant-current method lies slightly above the state of charge by the constant-potential method, since the latter approaches full charge asymptotically. When the curve representing the state of charge by the constant-current method begins to deviate from the ampere-hours actually put in by this method, it will be noted that a marked rise in the curve representing the ampere-hours wasted in gassing begins, and that this curve becomes parallel to the curve of ampere-hours input. The physical significance of the parallelism of these curves is that all of the ampere-hours supplied to the battery are eventually used in the decomposition of water. The curve representing the ampere-hours wasted in gassing by the constant-potential method shows that only a negligible part of the quantity of electricity passing through the cell is expended in this way. These curves also indicate that the constant-potential method of charging provides the maximum current input which the battery can absorb without the waste of energy in producing gas.

3. CHARGING AND DISCHARGING OF EDISON BATTERIES

The characteristic curves for charging and discharging the Edison storage battery of the type A6 are given in Figs. 75 and 76. The discharge curve resembles that for the lead battery, but the fall in voltage is somewhat more steep. The voltage curve on charge rises rapidly at the beginning and then more slowly until 5 hours have elapsed, following which the terminal voltage of the cell becomes constant at about 1.75 volts per cell. No specific gravity readings are recorded, since the electrolyte in these cells does not change in concentration during either the charging or discharging period. The temperature of the batteries rises markedly during both the charge and the discharge. In order that Edison batteries may give their full capacity on discharge, it is necessary that the charging rate should not be less than the normal rate specified by the manufacturer. Edison batteries gas throughout the entire period of charge.

These cells may be charged by the constant-potential or tapering-charge method, but this is not considered as satisfactory as the constant-current method for this particular type of battery. It is necessary that the average value of the current, if the tapering-charge method is used, should be equal to or greater than the normal constant-

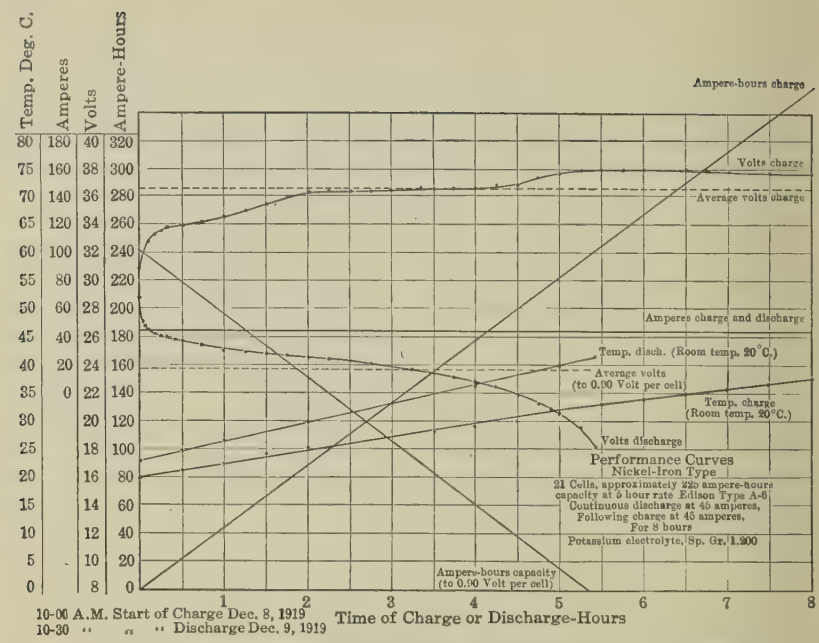

Temp. Deg. C.
Amperes
Volts
Ampere-Hours
Ampere-hours charge
Volts charge
Average volts charge
Amperes charge and discharge
Temp. disch. (Room temp. 20°C.)
Average volts (to 0.00 Volt per cell)
Temp. charge (Room temp. 20°C.)
Volts discharge
Performance Curves
Nickel-Iron Type
21 Cells, approximately 225 ampere-hours capacity at 5 hour rate Edison Type A-6
Continuous discharge at 45 amperes,
Following charge at 45 amperes,
For 8 hours
Potassium electrolyte, Sp. Gr. 1.200
Ampere-hours capacity (to 0.00 Volt per cell)
10-00 A.M. Start of Charge Dec. 8, 1919
10-30 " " " Discharge Dec. 9, 1919
Time of Charge or Discharge-Hours

FIG. 75.—Curves of discharge of an Edison battery, followed by charge by the constant current method.

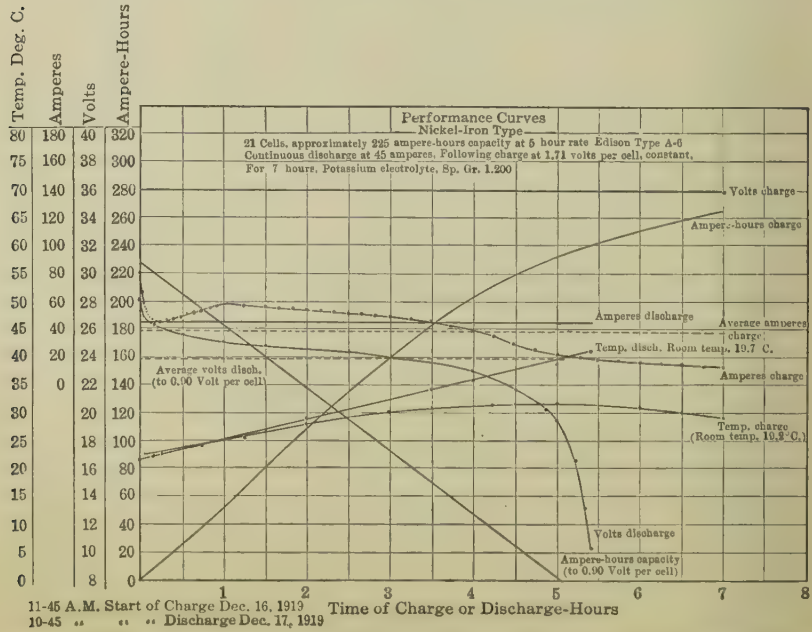

Temp. Deg. C.
Amperes
Volts
Ampere-Hours
Performance Curves
Nickel-Iron Type
21 Cells, approximately 225 ampere-hours capacity at 5 hour rate Edison Type A-6
Continuous discharge at 45 amperes, Following charge at 1.71 volts per cell, constant,
For 7 hours, Potassium electrolyte, Sp. Gr. 1.200
Volts charge
Ampere-hours charge
Amperes discharge
Average amperes charge
Temp. disch. Room temp. 19.7 C.
Average volts disch. (to 0.00 Volt per cell)
Amperes charge
Temp. charge (Room temp. 19.2°C.)
Volts discharge
Ampere-hours capacity (to 0.00 Volt per cell)
11-45 A.M. Start of Charge Dec. 16, 1919
10-45 " " " Discharge Dec. 17, 1919
Time of Charge or Discharge-Hours

FIG. 76.—Curves of discharge of an Edison battery, followed by charge by the constant potential method.

current charging rate, as otherwise the capacity of these batteries on discharge may be less than normal. Table XLIV gives the average voltages for discharge of various types of cells and Table XLV gives

TABLE XLIV

AVERAGE VOLTAGE, EDISON CELLS

(Computed for discharges of various types and sizes of cells at normal temperature to end voltages equivalent to 0.9 volt per cell at the normal rate. Normal rate for types A and B is 5 hours, for types G and J, $3\frac{1}{3}$ hours. Based on cells giving 113 per cent of their rated capacity.)

Multiples of Normal Rate	Average Voltage
$\frac{1}{2}$	1.26
1 (normal)	1.21
2	1.11
3	1.02
4	0.93

TABLE XLV

EDISON CELL VOLTAGES

(The voltages are for various types and sizes of cells discharging at multiples of the normal rate following normal charges and at normal temperatures. Normal rate for types A and B is 5 hours, for types G and J, $3\frac{1}{3}$ hours. Based on cells giving 113 per cent of their rated capacity.)

Per Cent of Rated Capacity Taken Out	Cell Voltages for Discharges Expressed in Terms of the Normal Rate					
	0.5	1 (Normal)	2	3	4	5
0*	1.51	1.47	1.39	1.31	1.23	1.14
0†	1.46	1.42	1.33	1.25	1.16	1.08
5	1.38	1.34	1.25	1.16	1.07	0.98
10	1.35	1.31	1.22	1.13	1.04	0.95
20	1.32	1.27	1.18	1.09	1.00	0.91
40	1.28	1.23	1.14	1.05	0.96	0.87
60	1.26	1.21	1.12	1.03	0.93	0.83
80	1.24	1.19	1.09	0.99	0.89	0.78
90	1.23	1.17	1.06	0.96	0.86	0.74
100	1.20	1.13	1.01	0.90	0.78	0.64
110	1.11	1.01	0.86	0.73	0.60	....

* Immediately following charge. † After standing 6 hours.

terminal voltages for varying amounts of discharge at various rates of discharge.

4. CHARGING EQUIPMENT

Except in the case in which d.c. bus-bars of suitable voltage are provided for battery charging, the charging equipment will ordinarily include a motor generator set, synchronous converter, or rectifier, to provide d.c. current at the proper voltage.

a. Motor Generator Sets.

It is not within the scope of this book to give any description of motor generator sets, but rather to give such information as may be required to plan the equipment which may be necessary in any particular case.

Kind of Power Available.—The first factor to be considered is the kind of power supply. If this is alternating current, it is necessary to know the voltage, the frequency, and the number of phases. If direct-current power is available, it is necessary to know the voltage and whether the supply lines are grounded or not.

Battery Data.—The batteries which are to be charged must be classified according to the number of batteries of each kind, the number of cells in each battery, the type of the battery, whether of the lead-acid or of the alkaline type, the capacity of the cells, and the purpose for which they are used. It is also necessary to know the maximum number of batteries which will be charged at one time, in order that the maximum capacity of the charging equipment may be calculated.

Charging.—The rate of charging will ordinarily be determined by the type of the batteries which are used. Starting and finishing rates are specified by the manufacturers of lead cells, and a fixed rate is also specified for each type of alkaline cells. If it is necessary to give the cells boosting charges, this fact should also be taken into account in computing the maximum capacity required of the charging equipment.

The method of charging, whether constant-current or constant-potential, must be chosen in advance, since generators of somewhat different characteristics are required for these methods. Generators for constant-current charging are ordinarily of the shunt-wound type with hand regulation capable of reducing the terminal voltage of the machine to one-half its normal value. The generators best adapted to the constant-potential charging are "flat" compounded machines which may be used without automatic regulators if an attendant is present. The question of resistances for modifying the constant-

potential method of charge must be considered in this connection, since the generators are calculated for the maximum capacity required of them during the early stages of the charging period (see p. 222).

Grouping of the Batteries.—The smallest batteries, particularly those for starting and lighting service, may be grouped in several different ways during charging. The most advantageous grouping will depend upon the capacity and the number of cells in each battery. Considering low-voltage batteries of 6, 8, and 12 volts, there is a choice of connecting them in parallel, in series, or in a combination of series and parallel. It is practical to charge these batteries in series up to bus-bar voltages of 115 volts, but higher voltages are not recommended for use in service stations, where the floors are often wet and the insulation not of the best. The series-parallel combination is the one ordinarily recommended. For this arrangement, bus-bar voltages of 37.5, 75, and 115 volts are convenient. Each circuit should be provided with a small ammeter and a regulating rheostat.

Sectional Panels.—Charging equipment can be obtained in the form of sectional panels, which are designed for any practical conditions or method of charging. The sectional panels include incoming line sections, generator control sections, and charging sections with resistors, both variable and fixed, voltmeters and ammeters, overload and underload circuit breakers, ampere-hour meters, reverse-current cutouts and fuses. If a proper selection of control panels is made, a convenient charging switchboard may be easily arranged.

b. Rectifiers.

Rectifiers for battery charging may be the electrochemical type, gas-filled bulbs, mercury arc, or the mechanical types.

In making measurements of the direct-current output from any of these rectifiers, it must be remembered that the direct current pulsates. The readings of direct-current instruments (D'Arsonval type) which give the average value of the current or voltage will not agree with the readings of alternating-current instruments which give the root-mean-square values. The amount by which the two kinds of instruments will differ will depend on the shape of the pulsating direct-current wave. In some cases the alternating-current instruments may indicate more than double the values of the direct-current meters. The process of charging a battery is governed by Faraday's law, and therefore the average value of the current is required, and direct-current meters should be used.

Electrochemical Rectifiers.—These consist of electrolytic cells containing two electrodes, one of which serves as a valve, permitting

current to flow in one direction but not in the other. Aluminum, tantalum, and a few other metals possess this peculiar valve action. During the operation of the rectifier, a film is formed on the surface of these metals that is permeable to hydrogen cations but not to the anions (Fig. 77), excepting those which act as " poisons " if present. The current can pass, therefore, to the valve electrode when it is the cathode, but not from it on the anodic part of the cycle, except at relatively high voltages when breakdown occurs. The time required to form this film depends on the voltage impressed on the rectifier and the area of the electrodes.

The electrolytes used in aluminum rectifiers are solutions of phosphates, borates, or tartrates, etc., but for tantalum rectifiers, solu-

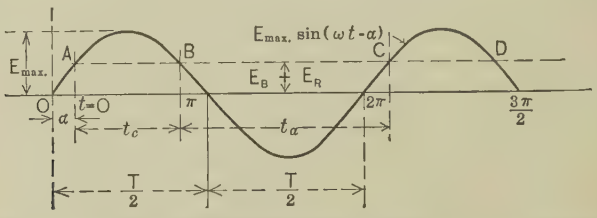


FIG. 77.—Relation of the impressed alternating voltage on an electrolytic rectifier to the battery voltage and the time that the valve is open. The valve is open from A to B, but closed from B to C during which time the rectifying metal is anodic. E_B, battery voltage and E_R, counter electromotive force of the rectifier.

tions of sulphuric acid of 1.250 sp. gr. are used. The other electrode may be lead, iron, or carbon. Carbon rods, if taken from dry cells, may contain enough chlorides to interfere with the operation of the rectifier, and it is necessary to clean them thoroughly before use. The voltage that the films can resist will depend on the metal, the solution, and its temperature. Aluminum can be used for higher voltages than tantalum, but the latter can be used at higher current densities. In some cases the maximum voltage which the aluminum film can withstand will reach 500 to 600 volts, but it is usually much lower.

The conditions for best operation of a chemical rectifier of this type are low temperature, low internal resistance, and the absence of impurities from the solution. Ions of chlorine, bromine, and nitrates destroy the valve action. The resistance of the cell may be decreased by properly shaping and placing the electrodes.

A single rectifier will rectify only one-half of the alternating-current wave, unless it is provided with three electrodes, one of lead or carbon, and two of aluminum, which act alternately as the cathode. The latter

arrangement is not always satisfactory because of the increased heating. It is, therefore, desirable to group four cells in accordance with the diagram shown in Fig. 78. The energy efficiency of the electrolytic rectifier under favorable conditions is about 40 per cent. Some commercial types of rectifiers are provided with incandescent lamps or wire resistances to provide current regulation. The efficiency is materially reduced by such an arrangement. Losses of energy in resistances may be avoided by the use of a small transformer to reduce the voltage to the required value or by the use of suitable choke coils. The efficiency for half-wave rectification (Fig. 79) is not materially lower than for the full-wave rectification. The degree of rectification is the ratio of the average direct current to the root-mean-square current. The theoretical maximum values for this ratio in a non-inductive circuit are 0.636 for half-wave and 0.905 for full-wave rectification. The maximum current for the ordinary sizes of aluminum rectifiers, such as may be made in jars of 1 liter (1 quart) capacity is about 1 ampere, but if the electrodes are artificially cooled, higher currents may be used. Tantalum rectifiers are now on the market and may be used for currents as large as three amperes.

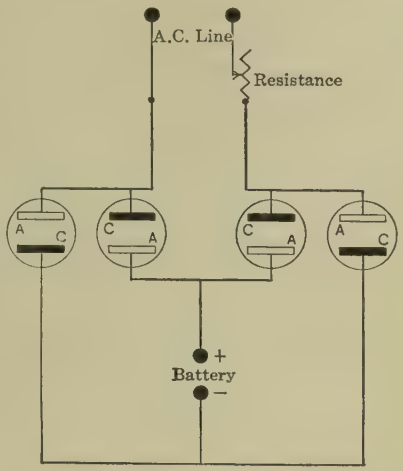


FIG. 78.—Four electrolytic cells arranged to charge a battery, rectifying both halves of the wave. *A*, aluminum; *C*, carbon.

FIG. 79.—Oscillograph record of the operation of an aluminum rectifier. Upper record, impressed emf; lower, rectified current, showing condenser current leading the emf by 90°. Leakage current, when present, is in phase with the emf.

Gas-filled Bulb Rectifiers.—A combination of a hot and a cold elec-

trode in a vacuum may act as a rectifier, because the hot electrode throws off electrons when it is charged negatively, and these, traversing the space to the other electrode under the influence of an electrostatic field, constitute an electric current. When the heated filament is positively charged, any electrons that are given off are immediately attracted back electrostatically to the filament, and no current can flow. An example of a rectifier of this type is the vacuum tube called the kenetron. Kenetrons operate on high voltages and relatively low currents. They are not suitable, therefore, for battery charging, but the rectifiers known as the "Tungar" and the "Rectigon," having bulbs which are filled with an inert gas, have been developed for this purpose. The inert gas, such as argon, in these bulbs becomes ionized by the electrons emitted by the cathode, and while ionized permits considerable current to flow through the tube. Ionization takes

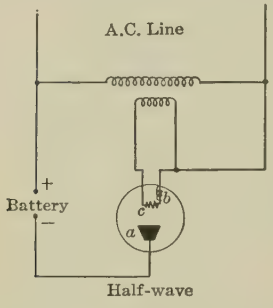


FIG. 80.—Gas-filled bulb rectifier.

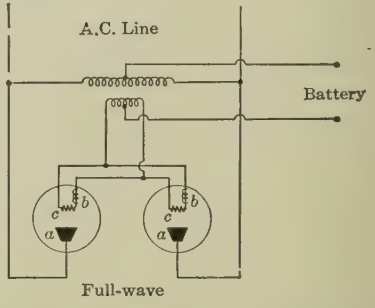


FIG. 81.—Gas-filled bulb rectifiers.

place only when the electrons stream out from the hot filament. During the other half cycle, the tube is closed to the passage of electric current. Most of the current which passes through the tube is carried by the ions from the gas, and only a relatively small part by the electrons. These tubes, therefore, operate on low voltages and will allow large currents to flow as compared with the vacuum bulbs. A bulb of this type is shown in Figs. 80 and 81, where (*a*) is the cold anode of graphite, and (*c*) is the hot cathode consisting of a spirally wound tungsten wire. A small ring of magnesium wire around the stem of the anode is included within the bulb to react with any gas (except the inert gas with which the tube is filled) which may be present and would otherwise impair the life and efficiency of the tube. This magnesium wire is called the "getter" and it is made to combine with the objectionable gases that may be present by a flashing process after the bulb is sealed. When this is done the anode is heated by an arc discharge which vaporizes a portion of the magnesium, and the products of the chemical combina-

tions are deposited on the inner surface of the bulb, giving it either a mirror-like or a sooty appearance. For this reason the bulbs are seldom clear, but this should not be taken to indicate that they are in

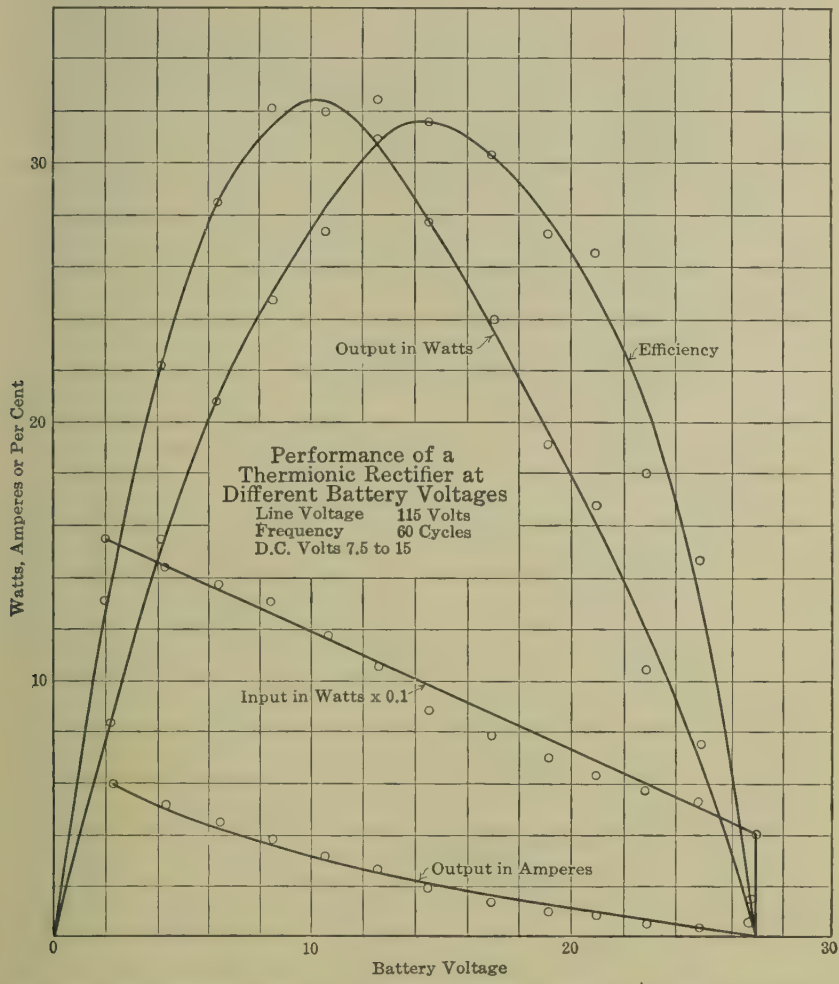


FIG. 82.—Characteristic curves of a gas-filled bulb rectifier. Curves of the same general shape may be drawn for any type of rectifier, but with different values of the coordinates.

bad condition. The connections for a bulb of this type to the alternating-current circuit are also shown in these figures. By using two tubes it is possible to rectify both halves of the waves. Some rectifiers of this type contain auto-transformers connected as shown, but varia-

tions in the connections will depend upon whether the secondary circuit is grounded or not. The small winding shown is a low-voltage, heavy-current coil supplying current to heat the filament. Characteristic curves are shown in Fig. 82.

Rectifiers of this type can be operated in parallel, if provided with suitable reactance. Two bulbs alone will not operate in parallel, since the one with the lower arc drop takes the load. The power factor is about 50 per cent.

The bulbs are made in the following sizes:

Current (Amperes)	Maximum Battery Voltage (Volts)	Rectification
$\frac{1}{2}$	45	Full-wave (2 anodes)
2	75	Half-wave
$2\frac{1}{2}$	75	Half-wave
5	75	Half-wave
6	75	Half-wave
30	45	Half-wave

The bulbs are mounted with transformers which are designed for specified voltages. Certain precautions should be observed in operating these rectifiers, to prevent damage to the bulb. The bulb, once started, will continue to operate without the cathode excitation, since the cathode can be kept hot by the bombardment of the positive ions. This does not eliminate the energy loss involved in heating the cathode, as the voltage drop across the arc increases. The arc tends to concentrate on a few turns of the filament when its normal excitation is cut off, and the filament will burn through at this point. It is not desirable, therefore, to operate the filament without its normal current, as the life of the bulb will be greatly shortened. If the battery voltage is 40 volts or more, both a.c. and d.c. circuits should be opened simultaneously by the rectifier switch, to prevent a possible surge of current through the bulb, which may happen when the a.c. circuit alone is broken. When such a surge occurs, a large current from the battery discharges through the bulb in the reverse direction, destroying it.

The efficiency of these bulb rectifiers may amount to 60 or 70 per cent when charging batteries of nearly the maximum voltages for which they are designed, but the efficiency decreases to less than 20 per cent when used for batteries of only a few cells. This is because the energy required to heat the filament and the energy loss in the arc itself, of

which the voltage drop is about 6 volts, become a large part of the total energy received by the rectifier from the alternating-current circuit.

Mercury-arc Rectifiers.—Mercury-arc rectifiers are particularly adapted to charging batteries of the vehicle type and others requiring larger currents than batteries of the starting and lighting type. The maximum capacity of the mercury-arc rectifier is 50 amperes, limited in practice by the inability to blow satisfactory bulbs which will carry heavier currents. Mercury-arc rectifiers in tanks, capable of carrying as high as 2000 amperes at high voltages, have been constructed in Europe, but they are not available commercially in this country.

A glass bulb containing mercury vapor will permit the electric current to flow in only one direction, to the cathode, but these bulbs are arranged to rectify both halves of the wave by providing two anodes. The anodes marked *A* and *A'* in Fig. 83 consist of graphite, and the third electrode, marked *M*, of mercury.

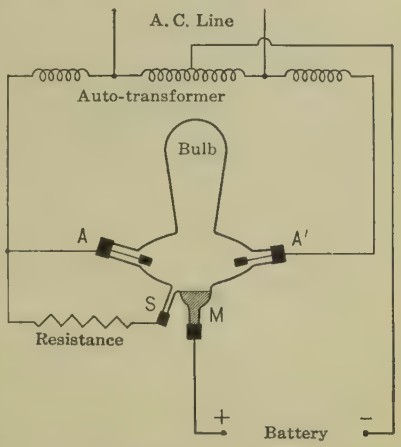


Fig. 83.—Mercury arc rectifier circuit. *A* and *A'* anodes; *S*, starting anode; *M*, mercury cathode.

In order to start a rectifier of this type, it is necessary to rock the bulb, which forms and then breaks a mercury bridge from the small starting anode, marked *S*, to the mercury cathode *M*. When the mercury bridge breaks, the cathode supplies ionized mercury vapor and this continues so long as the current is flowing toward the cathode. To prevent extinguishing the arc at the end of a half cycle, a large reactance is provided. The two anodes function in turn, the current flowing at any instant from the one which is opposed to the mercury cathode in polarity at that time.

Rectifiers rated from 10 to 50 amperes generally require a minimum current of from 5 to 15 amperes to maintain their arcs, but this can be reduced by adding sustaining reactance to a value of 4 or 5 amperes. Below these currents it is as economical and more reliable to maintain the vapor in an ionized state by means of auxiliary or "keep-alive" arcs acting similarly to the starting arc except that they operate on both halves of the wave continuously. For telephone and other "quiet" service, additional reactance is provided in the direct-current

circuit. Such outfits also use two-winding instead of auto-transformers.

Mercury-arc rectifiers are not self-starting as are those of the gas-filled tube type, but this feature can be added by using motor-drive or solenoid tilters, which are automatically cut out of circuit when the direct current starts to flow.

Mercury-arc rectifiers have an advantage over the gas-filled type and over motor-generator sets when operation for considerable periods at partial loads is necessary, since the light-load efficiency is substantially as good as that at full load. The efficiency increases as the direct-current voltage is raised.

Mechanical Rectifiers.—In the class of mechanical rectifiers may be included a wide variety of types, such as commutators driven by synchronous motors, vibrating reeds and switches, and the mercury-jet rectifiers of large current-carrying capacity. Since the use of mechanical rectifiers for battery charging is at present confined to low-rate charging of the small batteries which are used for railway signaling, starting and lighting of automobiles, and radio apparatus, the vibration type is the only one requiring consideration here.

The vibrating rectifier may best be described as a switch vibrating in synchronism with the alternating current, reversing the connection to the battery circuit as the alternating current reverses and maintaining a uni-directional pulsating flow of current to the battery. The vibrating element may be a pivoted armature, or the armature may be mounted on a spring. A variety of arrangements are on the market, but in any case the natural frequency of the vibrating member is of great importance for successful operation. It may vibrate with a frequency near that of the alternating current, or it may be designed to follow the impressed frequency as a forced vibration.

The vibrating armature is placed in the field of a permanent magnet and is actuated by the attractions and repulsions of one or more a.c. magnets during each half cycle of the alternating-current wave. An effort is made to adjust the motion of the armature, so that it shall make and break the connection to the battery circuit when the current flowing is zero or nearly so, in order to avoid sparking at the contact points. Various materials have been employed for the contacts, including platinum, tungsten, silver, and carbon.

These rectifiers are ordinarily used on 110–120 volt lines, and therefore a small transformer to reduce the voltage to the required amount is necessary. One terminal of the battery is connected to the secondary of this transformer, the other being connected through the contact points of the vibrating armature. A limiting resistance is provided

in the battery circuit to adjust the charging current to the proper value and to prevent a short circuit of the battery if the contact points should stick at any time. As additional protection, a small fuse in the battery circuit is desirable. The contact points must always be adjusted so that the battery circuit is open when the rectifier is not operating. The proper spacing of the contact points varies with the type of instrument, an average amount being perhaps 0.020 inch. The spacing does not regulate the voltage.

The requirements of railway service for this type of rectifier are particularly severe. Reliability of operation over considerable periods of time without attention is the first essential. The rectifiers are protected from the weather, but may be subjected to large changes in temperature and moisture. The insulation must be of the best. The vibrating member must remain in step with the alternating current throughout any ordinary fluctuations in frequency. The contacts must not be able to sustain an arc on the voltage across the gap; they must not be subject to oxidation or liable to weld together.

The efficiency of these rectifiers varies with the design of the instrument and the work that it is called upon to do. For this reason the rectifier should be used for the specific type of service for which it is designed. The efficiencies may vary from 10 to 50 per cent.

c. Ampere-hour Meters.

Since the ampere-hour is the unit commonly employed to measure the capacity of storage batteries, the ampere-hour meter is a convenient instrument for indicating the state of charge of such a battery. It may also be used to control or terminate the charge. Various types of ampere-hour meters have been developed, but the mercury-motor type is the most common form. This meter can be built as a rugged, dependable instrument which will keep in calibration and function satisfactorily even under severe conditions of service, such as may be encountered with mine locomotives, street trucks, or industrial tractors.

The ampere-hour meter performs two primary functions. In the first place, the meter hand will show at a glance how many ampere-hours have been discharged from the battery to which it is connected. Ordinarily, meters are supplied with a dial capacity slightly in excess of the total battery capacity. As the meter hand approaches the limiting capacity of the battery it shows the number of ampere-hours discharged, and consequently the remaining capacity which can be utilized before the battery must be recharged. This is valuable information in connection with any storage-battery installation, but par-

ticularly so with electric trucks, industrial tractors, or mine locomotives, as the driver can avoid being stalled with a run-down battery.

The meter has another important function; namely, that of controlling the charge. The recording train is constructed with a contact mechanism of the quick-acting type which can be installed at the zero or " full " point. This allows the battery to be put on charge with the assurance that when fully charged the contact will close, thus automatically terminating the charge. The contact wires are ordinarily connected to a shunt circuit breaker which breaks the main circuit. The meter is a safeguard against negligence and damage to the battery from over or under charging.

It is possible to incorporate two quick-acting contacts which are used for charging at two different rates. The auxiliary contact is commonly placed at the gassing point of the battery and introduces a resistance into the charging circuit which cuts the high starting rate down to the proper finishing rate. The ampere-hour meter, which actually measures the ampere-hours of electricity put into the battery, is an accurate and reliable method of maintaining a storage battery.

The mercury-motor type of meter consists of a copper disk immersed in mercury contained in a bakelite chamber. The current is taken in through a contact ear, passes across the disk and then out through a contact ear at the opposite side. Permanent magnets create a field cutting the disk, and rotation is produced on the well-known principle of Faraday's disk. Inasmuch as the field of the magnet is constant, the torque exerted on the moving armature is proportional to the current flowing.

Until 1924, the D-5 ampere-hour meter, as built by the Sangamo Electric Company, was the ampere-hour meter of the mercury-motor type in common use in the United States. This meter incorporated the mercury-motor principle as just described. It included also a second disk of aluminum on the same shaft as the copper disk. This rotated between the poles of the two permanent magnets and acted as a damper to retard the motion. The magnets induced eddy currents proportional to the speed in the disk and these, interacting within the field of the magnets, tended to retard the motion. The motor, therefore, can be used as a meter, since the speed of the moving element is proportional to the current flowing through the armature chamber.

The construction of their new type-N ampere-hour meter is different. A copper disk and similar mercury chamber are employed, but only one pair of magnets is used. These magnets are so situated that the pole tips are directly above and below the disk on opposite sides of the main shaft. When current is passed through the meter the disk

rotates. This rotation induces eddy currents in the same disk, as it cuts the magnetic field and damping is thereby accomplished.

In all mercury-motor meters the disk is practically suspended in the mercury, the pressure being upward against a cup jewel bearing. This construction allows the meter to be subjected to shocks and jars without damage. The type-N meter has a much higher torque than can be obtained with other types of construction. This is due to the magnets located in the base with the pole tips close together.

Adjustment of a meter of this type is accomplished simply by varying the shunt resistance by means of a small slider. Increased torque means increased accuracy, particularly at very light loads. The type-N meter with a simple shunt and no resistor element is built in capacities as low as $2\frac{1}{2}$ amperes. In the ordinary battery control meter which includes the resistor, the smallest capacity is 10 amperes. The range of accuracy of the meter is such that it will be practically correct at 5 per cent of full load or one-half ampere. All meters of this type will carry continuous overloads of 100 per cent without damage or material decrease in accuracy.

The ampere-hour efficiency of a storage battery is less than 100 per cent, and therefore a greater number of ampere-hours are required to charge it than were discharged previously. The efficiency depends on the construction of the battery, the rate at which it discharges, and the conditions of charging. It is possible to design the ampere-hour meter so that it will run slow during the charging period by a percentage that will be approximately equal to the difference between the efficiency of the battery under standard conditions and 100 per cent. The conditions of service must be carefully considered in determining the amount by which the meter should be retarded when running in the reverse direction. All Sangamo ampere-hour meters can, if desired, be furnished with the variable resistor element which allows the battery to be overcharged automatically by any desired percentage. The resistor is contained in a small bakelite box filled with mercury, in which a copper vane is located.

When the battery discharges, the resistance of this resistor is a maximum, and when charging, a minimum. The change in value of the resistance, as well as the adjustment of the amount, is brought about by the change in position of a copper bar immersed in mercury, relative to the current terminals. Copper has a much greater conductivity than mercury. The bar is rotated through a limited angle by the reaction of the field created by the passing of the current and the stray field of the permanent magnet of the meter. The bar swings one way or the other according to the direction of the flow of current

through the meter. It is necessary, of course, to determine what percentage of excess charge should be given the battery, the ordinary setting being 20 per cent for lead batteries and 25 per cent for Edison batteries. The resistors are always calibrated to show percentage of excess charge. In some of the earliest types of ampere-hour meters, a distinction was made between the percentage slow on charge and percentage of excess charge, which are not the same. For example, if the meter ran slow on charge by 25 per cent, the battery received 33 per cent excess charge. All meters are now scaled to show percentage of excess charge.

The normal speed of a Sangamo meter at its rated current is 10 revolutions in 36 seconds, from which it is at once apparent that one revolution represents a number of ampere-seconds equal to 3.6 times the number of amperes flowing. Thus, if the rated current is 10 amperes, one revolution corresponds to 36 ampere-seconds, and if the current is 60 amperes, the revolution corresponds to 216 ampere-seconds. The value of the ampere-seconds per revolution is the so-called constant of the instrument, which we may designate by K. Letting N equal the number of revolutions, I the current in amperes, and T the time in seconds, the number of ampere-seconds corresponding to N revolutions at a current I becomes

$$IT = KN. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Ampere-seconds may be converted into ampere-hours by the relation

$$3600 \text{ ampere-seconds} = 1 \text{ ampere-hour.}$$

To calibrate an ampere-hour meter by the use of a calibrated ammeter and stop-watch, it is necessary to time some arbitrary number of revolutions when a steady current at a specified rate is flowing through the meter. By the equation above, the time for N revolutions when the current is I should be

$$T = \frac{KN}{I}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If, however, the time is found to be T_1, the percentage error may be calculated from T and T_1. When the meter is slow there will be too few revolutions in a given interval, and when it is fast, too many. The percentage by which the meter is slow or fast is the ratio of the number of revolutions actually made in a given time to the number that should have been made. Since the speed of the revolutions is inversely as the time interval, we may calculate at once the percentage by which the

meter is slow or fast from the ratio $\frac{T}{T_1}$ where T_1 is observed and T determined by Formula (2).

Ampere-hour meters have been used for a great many purposes. Possibly the best-known installation is on commercial electric trucks, practically all of which are now equipped with ampere-hour meters at the factory. A typical wiring diagram of ampere-hour meter control is shown in Fig. 84. Electric pleasure vehicles as well have been equipped with ampere-hour meters. The type-*N* meter can be installed successfully on industrial trucks and tractors, which are subjected to very rough service. Practically all of the storage-battery mine locomotives in the country are equipped with ampere-hour meters,

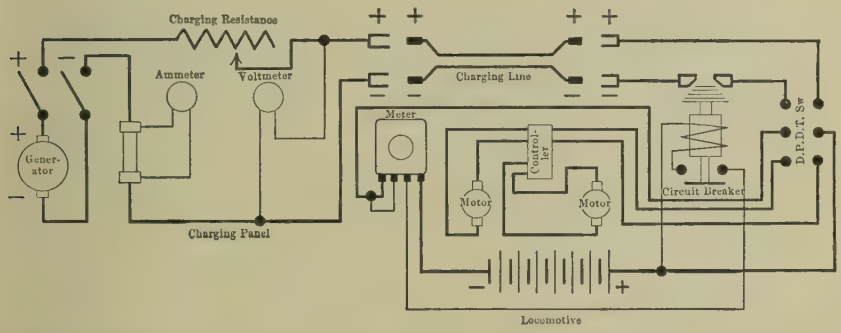


FIG. 84.—Typical wiring diagram of ampere-hour meter control of battery truck charging with shunt trip circuit breaker on the truck.

both for indicating the state of battery charge and for control of the charge.

Another well-known installation is in connection with railroad train lighting batteries. Many Pullman cars are equipped with an ampere-hour meter, and a large percentage of other electrically lighted cars are so equipped. In a number of cases the meter is used as a control device, so that when the battery reaches the full point the contacts operate to cut down the generator voltage to the point at which the battery will float. Other meters are merely used as indicating instruments which will allow the inspector to see at a glance the condition of the battery.

Meters have been installed on submarines of the United States Navy and other navies, including those of Spain and Japan, for control of the batteries. Some radio batteries are provided with ampere-hour meters, where a failure of the current might be disastrous.

5. BATTERY REGULATION

In the preceding portion of this chapter, the voltage characteristics of the storage battery on charge and discharge have been discussed. The terminal voltage of the cells decreases during discharge and increases during the charging period. It is necessary to compensate for these changes when the battery is used to maintain the potential of bus-bars in power circuits. When the current flowing in the circuit is very small, this regulation is satisfactorily accomplished by the use of a regulating resistance. With cells of large capacity this would be a very wasteful and inconvenient method, and other methods must be employed. These may be classified as follows: end cells, counter cells, boosters, and methods of alternating-current regulation.

End-cell Regulation.—The falling voltage of a battery on discharge may be compensated for by adding additional cells from time to time. The name "end cells" comes naturally from the familiar arrangement of providing taps to each of a limited number of cells at the ends of a battery, so that any of these may be connected or disconnected at will without interrupting the flow of current from the battery to the bus-bars. Figure 85 shows a simple diagram of such an arrangement for a three-wire circuit. If the battery is to be connected to the bus-bars only during discharge or when floating on the line, a single end-cell switch at each end of the battery is all that is ordinarily required. If, however, the battery is to be floated on more than one set of bus-bars, end-cell switches are required for each set. In rare cases, the battery will be required so continuously on the bus-bars that it must be charged while maintaining a constant bus voltage. In such a case, additional end-cell switches are required.

The successful regulation of voltage by the use of end cells requires well-designed switches. These switches must not interrupt the connection between the battery and the bus-bars, nor short-circuit any cell when the switch is being operated. The switch must be capable of carrying the maximum current of the battery. The switches must also be free from heating and sparking at the contacts. Small switches are hand-operated, but the larger ones are motor-driven and are often automatic.

The number of end cells which is required is calculated from the maximum voltage drop and the total number of cells in the main battery. In the simplest case, the initial discharge voltage may be assumed to be 2 volts per cell, decreasing as the cells discharge to 1.8 volts per cell, or 10 per cent. At least one end cell to each ten cells in the main battery is therefore required. If the battery is to be charged while on

the line, additional end-cell connections will be necessary. The cells will increase to about 2.60 volts per cell, or 30 per cent, which, added to the 10 per cent required for discharge, makes a 40 per cent variation in voltage to be compensated for by the end cells. The actual number in any case can be calculated only when full data of the service are available. End cells are cut out on charge and in on discharge. In large stand-by batteries for central-station service it is not customary to provide enough end cells to maintain normal bus voltage during a heavy emergency discharge, and it frequently happens in such a case that all of the cells are cut in immediately and the bus voltage allowed to drop where it will as the discharge continues.

End cells are usually of the same size as those in the main battery, although they are seldom used as much. The last cell cut in on discharge

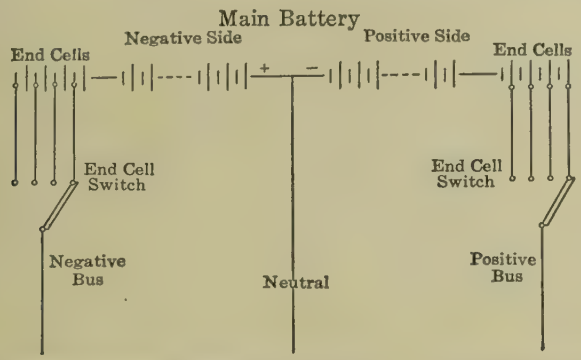


FIG. 85.—Arrangement of end cells in a battery. For a two-wire circuit the end cells are at one end only.

obviously delivers only a small portion of the ampere-hours delivered by the cells in the main battery. They are consequently charged in a shorter time and must be cut out of the circuit when the charge is complete.

Counter Cells.—A second method of voltage regulation is by counter cells. Counter cells are provided with grids or unformed plates in place of the regular plates. They have no capacity, but develop a potential of 2.3 to 3.0 volts, depending on the current flowing, which opposes the potential of the main battery. Like end cells, the counter cells are placed at the outside ends of the main battery, and each cell is wired separately to a switch which permits the successive cells to be cut out of the circuit at will. Unlike end cells, however, the counter cells are cut out of the circuit as the voltage of the main battery falls, because their effect is subtractive instead of additive.

Applications of counter cells have been made to batteries which do not float on the line. It is not advisable to allow the current to reverse its direction through the counter cells, because the reversals would result in Planté formation of the plates or grids and build up their capacity. The chief value of counter cells lies in their lack of capacity, which enables them to acquire their full counter electromotive force almost instantaneously after being thrown on the line. The counter cells should be cut out of the circuit when the main battery is on charge, unless they are used to absorb the excess voltage of a charging circuit when they are cut out during the discharge of the main battery.

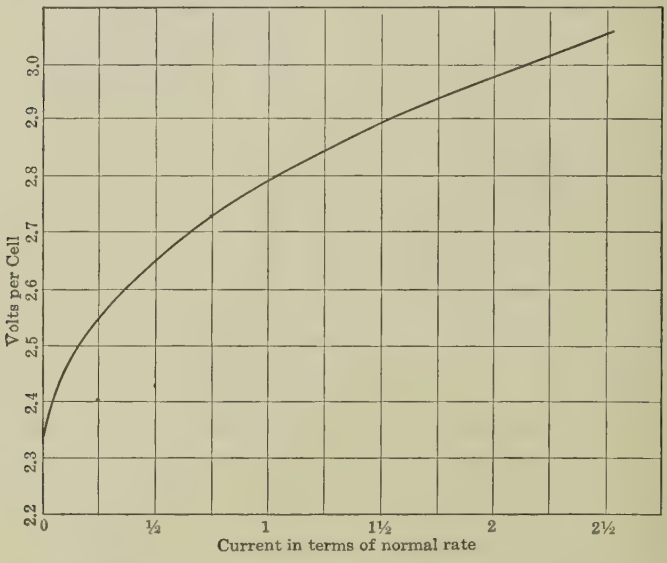


Fig. 86.—Relation of voltage of counter cells to the current.

The voltage by which the counter cells oppose the voltage of the line varies somewhat with the size and construction of the cells, as well as with the current which passes through them. Figure 86 shows the terminal voltage per counter cell for cells of the stationary type having plates $7\frac{3}{4}$ by $7\frac{3}{4}$ inches. The curve is made applicable to the general case by expressing the current in terms of the normal 8-hour current, taken as unity, for the regular cells (with formed plates) of the same size and number of plates.

The use of counter cells is by no means as common as the use of end cells for voltage regulation. The advantages which they possess over the end cells are the following: (1) all of the cells in the main

battery are worked equally on both charge and discharge; (2) the cells provide a cushioning action, so that the battery may be thrown on the line even when the battery voltage is considerably in excess of the bus voltage. Counter cells possess the following disadvantages as compared with end cells: (1) counter cells represent an additional investment, since the number of active cells is reckoned as the total number required, including what would otherwise be the end cells; (2) the energy dissipated in the counter cells produces heat and the decomposition of water, which means a large amount of gassing; (3) the minimum number required is not as definite as in the case of end cells, because of the large voltage variation depending on the operating conditions; (4) the grids require renewal at intervals, depending on the amount of use. Counter cells are of less importance now than formerly.

Boosters.—A third means of regulation is by the use of boosters. In the Standardization Rules of the American Institute of Electrical Engineers, a booster is defined as a generator inserted in series in a circuit to change the voltage. The booster is usually motor-driven, and in such a case it is designated as a motor-booster. A wide variety of boosters are available for various purposes. These include (1) charging boosters used in connection with storage batteries, which discharge into a line and require the addition of a small voltage to the line voltage to complete the charge of the battery; (2) automatic regulating boosters for constant current or constant voltage, to take care of rapid fluctuations in the line; (3) separately excited differential boosters whose fields are excited and controlled either by the action of a solenoid, carrying the main-line current, on a pair of carbon piles, or by an auxiliary exciter machine whose field is excited by a portion of the main-line current. In either case, the field of a differential booster at any time will determine the amount and polarity of its voltage.

An interesting application of the differential booster is found in the service of the third-rail system of a large railroad, for which a battery of over three hundred cells, 4000 ampere-hours, is provided to carry the peak load and provide for emergencies. The service of the battery is regulated by the help or opposition of the booster. The booster is in series with the battery on the negative end, and it is excited by a second machine whose field is shunted by an automatic carbon regulator which may reverse the exciter current and so cause the booster to help or buck the battery according to the traffic.

The use and application of boosters to storage-battery regulation has been so fully described in the various handbooks and textbooks of electrical engineering and in Lyndon's " Storage Battery Engineering " that a detailed discussion of them will not be attempted here.

Alternating-current Regulation.—Although the storage battery is a direct-current apparatus it has found some application to the regulation of alternating-current systems. Examples of such systems are the following: (1) railroad electrification with alternating-current transmission lines in which the movement of heavy trains causes abnormally high loads as compared with the average load; (2) cases where alternating-current power in considerable quantity is purchased on a maximum demand basis; (3) cases where the auxiliary apparatus used with the storage battery can be used to advantage to change the frequency or control the power factor; (4) distribution systems with heavy and fluctuating loads in industrial plants.

If the distribution system is alternating-current, but the load direct-current, the application of the battery may be at the point where the load is required and may consist of the usual arrangement of batteries with end cell or booster control. If, however, the load is alternating-current, conversion apparatus, such as motor generators or synchronous converters, are necessary in the battery circuit. Reference is made to an extended discussion of the application of storage batteries to the regulation of alternating-current systems, by Woodbridge.[3]

6. OPERATING CONDITIONS

a. Safety-code Requirements.

Rules relating to the installation of stationary batteries exceeding 50 kilowatts capacity at the 8-hour rate of discharge (except 133) are provided in the National Electrical Safety Code, Section 13.[4] These rules are as follows:

130. Isolation.

Storage batteries shall be made inaccessible to other than properly qualified persons by being placed in a separate room or inclosure.

131. Ventilation.

Rooms or inclosures containing storage batteries shall be so ventilated as to remove acid spray and prevent dangerous accumulation of inflammable gas

The battery-room ventilating system shall be so arranged as not to carry any gases therefrom into other rooms or spaces of the building where electrical apparatus or equipment is located.

Communication of drafts to other rooms should be prevented.

[3] Trans. Am. Inst. Elec. Eng., 27, p. 987, 1908.

[4] National Electrical Safety Code, 3rd ed., Handbook Series of Bureau of Standards, No. 3, 1920.

132. Suitable Supports and Floors.

The cells, except small cells of insulating material set in sand trays, on shelves, or otherwise separated from the floors, shall be supported by suitable insulators, such as glass or thoroughly vitrified or glazed porcelain. Suitable drainage or other means shall be provided beneath the cells to prevent the accumulation of electrolyte in case of leakage or spraying.

Acid-resistive floors, such as vitrified brick set in pitch, are recommended where large batteries are installed.

133. Guarding Live Parts in Battery Rooms.

(*a*) *Separation of Parts of More than 150 Volts.*—The arrangement of cells and connections shall be such that any two current-carrying parts between which a voltage exceeding 150 exists shall be properly guarded if the parts are otherwise so exposed that persons are liable to make accidental contact with both at the same time.

(*b*) *Precaution against Parts of More than 150 Volts.*—No conductor of more than 150 volts to ground shall be placed in any passageway, unless guarded or isolated by elevation.

134. Illumination.

Storage-battery rooms should be lighted, if practicable, from outside lamps. Heating devices with open flames or exposed incandescent resistors shall not be installed. If lamps are inside, only incandescent lamps in keyless porcelain or composition sockets, controlled from points not exposed to battery vapor, shall be used. It is recommended that switches and incandescent lamps located in battery rooms be put in vapor-proof containers.

135. Acid-resistive Coverings.

Conductors in battery rooms, if of such material or so located as to be liable to corrosion, shall have suitable protective coverings or coatings, unless the ventilation is such as to render this unnecessary.

b. Care of Rooms.

Aside from the proper installation of the batteries, the care of the rooms constitutes an important factor in their successful operation. The moisture and the acid spray that are necessarily present increase the amount of care required over that which is necessary for other electrical equipment.

Ventilation.—The objects in providing ventilation for storage-battery rooms and compartments are three. The first is to carry off the gases which are liberated during the charging period and to some extent by the negative plates at other times, since the hydrogen constituent of the gas forms an explosive mixture with the oxygen of the air. The second object of ventilation is to preserve the insulation of the installation by carrying off the acid spray, which is destructive to woodwork, most kinds of paint, and insulating materials. The third object of ventilation is to cool the batteries during the charging periods

and when working under heavy loads. This is of particular importance in the case of batteries in closely confined compartments, as on submarines and on certain industrial trucks. Forced ventilation is desirable in all cases where the natural draft is small or unreliable. As the gassing and maximum temperature occur near the end of the charge, it is customary in some installations to provide only moderate ventilation during the early stages of the charge and then increase the ventilation after the battery has received about 75 per cent of its charge. The full ventilation should be continued for a considerable time after the completion of the charge. A 4 per cent mixture of hydrogen in the air is dangerous, and because of its lightness hydrogen tends to accumulate in the top of the room or compartment. The amount present at any place should not be allowed to exceed 2 per cent.

Insulation.—In addition to the ventilation, certain other precautions are necessary to preserve the insulation. The supports for the tanks should be porcelain or glass insulators with oil cups. All metal except lead should be protected against acid spray. The overhead wiring should be carried on porcelain insulators which are easily accessible so that they can be wiped off from time to time. The heads of the screws in the insulators should be covered with vaseline. In some large installations the copper bus-bars and other cables are inclosed in a lead sheathing. The floors should be of water-proof material with drain at the lowest point so that they can be flushed with the hose. About twice a year the floors should be scrubbed with bicarbonate of soda solution. After the flushing, the floors should drain quickly and dry without water pockets.

c. Record Forms.

Accurate records of the performance of the large stationary batteries and certain of the smaller batteries, such as vehicle and train lighting batteries, are desirable. The records indicate sources of trouble in the early stages, and they provide the necessary data for comparison of different makes and types, as well as for making an accurate computation of the cost of operation. The forms to be used will naturally depend upon the service and to some extent upon local conditions, but the following have been in successful use and are given by way of illustration.

The first (Form 1) is applicable to the batteries in industrial trucks and tractors. It was used at a large shipping depot during the war. The second (Form 2) is a good form for keeping a record of the fluctuations of the specific gravity of any kind of battery, but it was designed primarily for a stationary battery. The third form (Form 3) is for a

STORAGE BATTERY RECORD FOR THE MONTH OF _____

Depot _____ At _____ Date in service _____

Battery of _____ cells. Type _____ Battery No. _____

DAILY READINGS—DIRECTIONS: Start Charge as given in the Methods Bulletin recording time and amperes. Select a conveniently located cell as a pilot cell, and immediately after the daily charge is completed record the specific gravity and temperature of this cell. Once every week give battery an equalizing charge; replace evaporation with pure water before the charge is started. Note on reverse side of sheet any unusual condition or attention given the battery.

Date	BOOST				REGULAR CHARGE AT END OF DAY						
	START		FINISH		START OF CHARGE			END OF CHARGE			
	Time	Amp.	Time	Amp.	Time	Amp.	Sp. Gr.	Time	Amp.	Sp. Gr.	Temp.
1											
2											
3											
4											
5											
6											
7											
8											
9											
28											
29											
30											
31											

Monthly or Individual Cell Reading Directions:

Once each month immediately after an Equalizing Charge, take and record Sp. Gr. of each cell in the battery.

Sp. Gr. Taken _____ A.M. P.M.

Voltage Taken _____ A.M. P.M.

Charging Amps. while read. Volt _____

Date _____

Cell	Sp. Gr.	Volts	Temp.
1			
2			
3			
22			
23			
24			

WEEKLY OR EQUALIZING CHARGE READINGS—DIRECTIONS: Once every week after the daily charge has been completed give the battery an equalizing charge (see Methods Bulletin) and record readings called for at half-hour intervals, below. Note any cells that do not gas as freely as the rest, on the reverse side of sheet.

DATE _____

Time	Amps.	Volts	Sp. Gr.	Temp.

DATE _____

Time	Amps.	Volts	Sp. Gr.	Temp.

DATE _____

Time	Amps.	Volts	Sp. Gr.	Temp.

DATE _____

Time	Amps.	Volts	Sp. Gr.	Temp

WATER ADDED

REMARKS.

READINGS TAKEN BY

FORM 1.—Record sheet adapted for use with a truck, tractor, or vehicle battery.

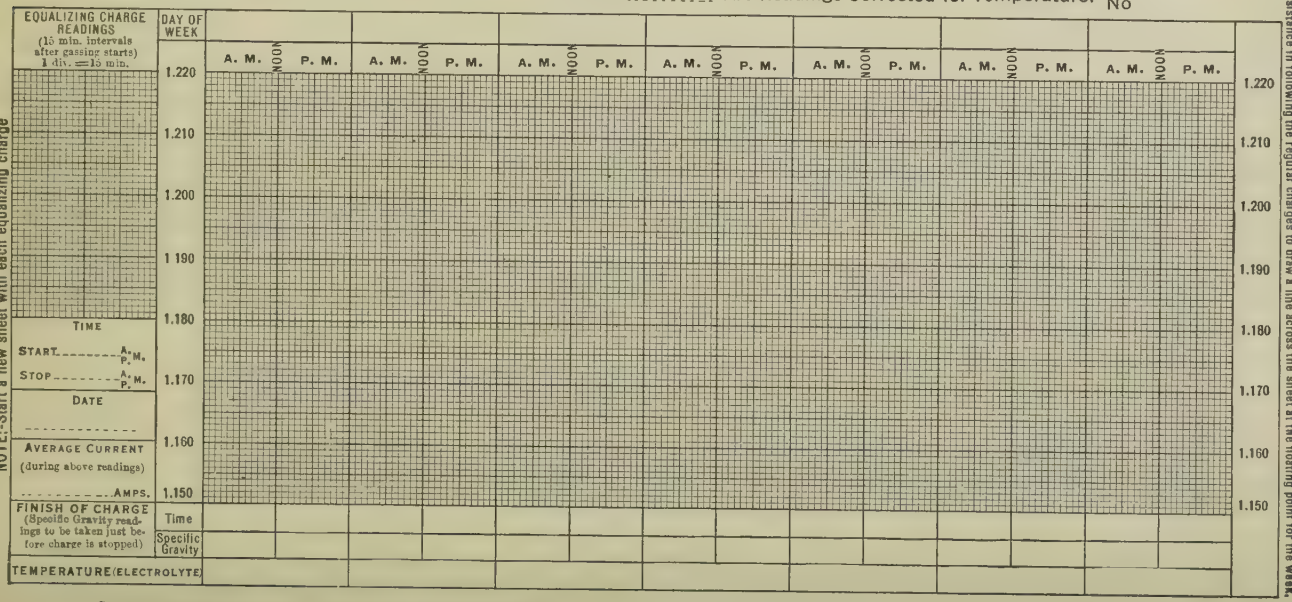
PILOT CELL SPECIFIC GRAVITY READINGS

Plant of_____ Located at_____ Battery No._____

Week Beginning_____ 191____ Cell No._____ Are Readings Corrected for Temperature? Yes No

NOTE:-Start a new sheet with each equalizing charge

NOTE:-It is of assistance in following the regular charges to draw a line across the sheet at the floating point for the week.



READINGS TAKEN BY_____

FORM 2.—Record sheet for pilot cell readings.

REPORT ON BATTERY PLANT

Plant of _____ At _____

Number of Cells _____ Type _____

Temperature of electrolyte _____ °F. of battery room _____ °F. Charging Current _____ amperes. Voltage readings to be taken if possible at end of charge with current still flowing. Take gravity readings immediately after voltage readings. If on regulation during readings, current fluctuations were from _____ amp. charge to _____ amp. discharge.

POSITIVE SIDE									NEGATIVE SIDE									
Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr.	Cell	Volts	Sp. Gr.	REMARKS
1			41			81			1			41			81			
2			42			82			2			42			82			
3			43			83			3			43			83			
4			44			84			4			44			84			
36			76			116			36			76			116			
37			77			117			37			77			117			
38			78			118			38			78			118			
39			79			119			39			79			119			
40			80			120			40			80			120			

Specific Gravity Readings by _____ A.M. P.M. _____ (Date)

Voltage Readings by _____ A.M. P.M. _____ "

Ampere Hour Meter Reading _____ Charge _____ Discharge. Constant of Meter _____

Watt

Water added to replace Evaporation _____ (Date) _____

Cells late in gassing on overcharge, Positive side _____

_____

Cells late in gassing on overcharge, Negative side _____

_____

FORM 3.—Record sheet for a stationary battery.

stationary battery and includes the readings that should be made at the close of each equalizing charge.

7. COSTS OF OPERATION

It is often important to make an accurate estimate of the cost of operation of trucks, tractors, or vehicles, and an outline of the general method, taken from Circular 92 of the Bureau of Standards, is given below. The example which is given is purely illustrative. The prices for the battery, its parts, and the labor were perhaps approximately correct at the time the example was prepared. These are subject to changes, however, and the example must therefore be considered as an outline of the method rather than as the estimate for a particular installation.

The following example illustrates the method of computing the cost of operation of a battery for an industrial tractor. It suggests the method to be followed in making a similar estimate for other types of storage batteries.

An estimate of the cost of operation is usually made for the purpose of determining the economy of a battery installation or of comparing one type of battery with another, to meet a given condition of service. In making such an estimate, the following items must be taken into consideration:

Equivalent batteries must be compared, that is, batteries having approximately the same watt-hour capacity at the service rate of discharge.

Interest must be paid on the investment, which is the cost of the initial battery and the renewals.

Depreciation is the amount of the capital investment to be written off per year, and is equal to the total investment in the battery divided by the number of years for which the cost of operation is to be estimated. At the close of the period, the battery last in service may have a small scrap value. The amount of money set aside each year for depreciation is a sinking fund to amortize the debt.

The **watt-hour efficiency** of the battery is to be used in computing the cost of power for charging.

The **life** is the period of useful service, usually expressed in years.

The quantity of **electrolyte** is that required for renewal, or to replace losses by leakage, etc.

The quantity of **water** is that required to replace the losses by gassing on charge, that is, the quantity decomposed by the ampere-hours of charge exceeding 100 per cent of the previous discharge. It is, therefore, dependent upon the ampere-hour efficiency of the battery.

The quantity of **power** required is that for charging, expressed in kilowatt-hours.

Cleaning for lead batteries includes renewal of wood separators, trays, and minor parts. This is seldom required now.

Labor is that required for normal maintenance. It depends on the size and kind of battery.

Example.—Assume a battery of the lead-acid type of 24 cells, as follows:

Capacity	ampere-hours	225
	kilowatt-hours	10.5
Average voltage on discharge	volts per cell	1.95
Watt-hour efficiency	per cent	75
Ampere-hour efficiency	per cent	90
Life	years	2.5
Initial cost	per cell, complete	$30.00
Renewal cost	per cell, complete	$25.50
Jars	each	$ 4.00
Covers	each	$ 1.00
Wood separators	each	$ 0.04
Intercell connectors	each	$ 0.35
Wood trays	per cell	$ 1.66
Period for which estimate is made	years	10
(This will require one initial battery and three renewals)		
Rate of interest	per cent	6
Cost of initial battery		$720
Scrap value, 15 per cent		$108
Cost of renewal		$612
Efficiency of charging system (synchronous converter)	per cent	88
Working days per year		300
Cycles of charge and discharge	per day	1

Interest:

Initial battery	$720 \times 0.06 \times 2.5 =$	$108.00
First renewal	$612 \times 0.06 \times 2.5 =$	91.80
Second renewal	$612 \times 0.06 \times 2.5 =$	91.80
Third renewal	$612 \times 0.06 \times 2.5 =$	91.80
Total interest		$383.40
Per year		38.34

Depreciation:

Initial battery	$720.00
Three renewals, at $612	$1836.00
Total investment	$2556.00
Scrap value	$ 108.00
Net investment	$2448.00
Per year	$244.80

Electrolyte:

None required for lead batteries except to replace loss by spillage or leakage, which is negligible if battery is properly cared for.

Water:

Assumed daily charge to be at 90 per cent efficiency.

$\frac{225}{.90} = 250$ ampere-hours input.

Excess of input over normal capacity 25 ampere-hours, $25 \times 300 = 7500$ ampere-hours per year.

Equalizing charge weekly for 30 ampere-hours excess, $30 \times 52 = 1560$ ampere-hours.

$7500 + 1560 = 9060$ ampere-hours total input exceeds output.

One ampere-hour decomposes 0.336 gram (0.01185 ounce) of water, whence 9060 ampere-hours will decompose 3044 grams (107.4 ounces) per cell. As there are 24 cells the total water consumption will be 73 liters (19.3 gals.). For distilled water at $0.10 per gallon the expense will be $1.93.

Power:

The input per day is $\frac{10.5}{0.75} = 14$ kilowatt-hours.

The energy, allowing for losses in the charging outfit, is $\frac{14.0}{0.88} = 15.92$ kilowatt-hours.

The energy used per year is, therefore, $15.92 \times 300 = 4776$ kilowatt-hours per battery. A $0.02 per kilowatt-hour the cost of charging is $95.52 per battery per year.

Labor:

One battery man, at $200 per month	$2400
Two assistants, at $25 per week	$2600
Total, per year	$5000

As this is sufficient for 10 tractors, the proportionate cost for one is $500, of which about $\frac{1}{2}$, or $250, is chargeable to the batteries.

Summary:

Interest	$ 38.34
Depreciation	244.80
Water	1.93
Power for charging	95.52
Labor	250.00
Total cost of operation per battery per year	$630.59

8. DISMANTLING AND ASSEMBLY OF LEAD-ACID TYPE

First, clean the top of the battery thoroughly.

Before starting to dismantle the battery, make a sketch or diagram showing the relative locations of cells, intercell connectors, terminals, and any other data necessary to insure the correct assembly.

a. Removal of Connectors.

(*a*) **Connector Puller.**—Remove the filling plug on the cell to be dismantled and place the puller in position. With the puller vertical, screw the plunger down gradually until the connector is free from the post (see Fig. 87). This method is quick and easy, eliminates boring out, but necessitates trimming the posts for reassembly of the cell.

FIG. 87.—Use of the connector puller. The vent plug must be removed.

(*b*) **Boring Out.**—Bore out the connector, using a brace and bit. The bit may be either a twist drill or a wood bit, the latter preferred, and should be at least as large as the post, usually $\frac{5}{8}$ inch (1.6 cm.) or $\frac{3}{4}$ inch (1.9 cm.). Before boring, the bit should be centered carefully on the connector. The hole should be bored to a depth of about $\frac{3}{16}$ inch (0.5 cm.). The filling plug should be in position while boring out, to prevent lead chips getting into the cell (see Fig. 88). When the hole has been bored to the proper depth, the connector will seem loose and the joint between the connector and the post can be seen. After boring out the connector, insert a screw driver between the underside of the connector and the sealing nut, if there is one, and pry firmly but gently on the connector. Repeat this operation on the other side of the post and continue until the connector is free (see Fig. 89). If there is no sealing nut which can be used as a brace for prying up the connector, place a heavy strip of wood across the top of the cell next to the post

and use this as a brace. Care should be taken not to put pressure on the cover. If the boring out of the connector is not done properly—for instance, if the hole is not concentric with the post—heat can be

FIG. 88.—Boring out the connector. The bit must be carefully centered.

applied gradually to the connector until the lead is softened sufficiently to permit pulling up the connector with a pair of pliers.

In all of the above operations, care should be taken not to short-circuit the cell by allowing pliers or other tools to come in contact with both posts at the same time.

b. Removal of Cell.

Grasp each post with a pair of pliers and pull vertically (see Fig. 90). If the jar sticks, a hot putty knife may be inserted around the edges. This will usually loosen the jar so that it may be pulled out easily. After the jar has been pulled out, rest it on the edge of the tray so that the pliers may be removed and the cell lifted by the hands to a position for the next operation.

FIG. 89.—Prying off the connector after boring it out. Care must be taken not to break the cover.

It is to be noted here that the positive post has more corrosion than the negative.

The sealing nuts, if used, should be removed next by means of a special wrench. If such a wrench is not available, use a pair of pliers, and only as a last resort use a monkey wrench or a pipe wrench (see Fig. 91). Note the shape of pliers used. The sealing nuts are sometimes held in place by scoring the threads on the post with a prick punch.

c. Removal of Element.

With the filling plug out, blow the gases out of the cell. This is to reduce to a minimum the possibilities of an explosion. Warm the

FIG. 90.—Removal of cell from the battery. If the jar sticks a hot putty knife may be inserted around the edges.

FIG. 91—Removal of the sealing nut.

outside of the jar at the top with a flame and then insert a hot putty knife around the inner edge of the jar, melting out the compound to a depth of about $\frac{1}{2}$ inch (see Fig. 92). This operation should be performed as rapidly as possible, as the compound cools quickly. Next, place the finger in the filling aperture and lift vertically on the cover. If the cover does not pull readily, remove all of the sealing compound possible by means of the hot putty knife and reheat the sides of the jar before again pulling on the cover.

Fig. 92.—Cutting out the cover with a hot putty knife. Before doing this the gases should be blown out of the cell to avoid a possible explosion.

After the cover has been removed, clean it thoroughly and wipe off the edges, where sealing compound is to be poured, with a cloth damp with dilute ammonia or bicarbonate of soda.

Place the jar, with the cover removed, on the floor with one foot on each side and grasp each post with a pair of pliers. Pull the element upward while holding the jar with the feet (see Fig. 93). When the element is nearly out, place it slightly out of plumb on the top of the jar and let it drain for about five minutes (see Fig. 94). The element should not remain out of the jar for more than fifteen minutes on account of injurious heating. Should the negative plates begin to dry out and heat, sprinkle them with water until they can be taken care of.

d. Removal of Separators.

Place the element on the edge of a table or bench. When it is necessary to use the separators again, it is desirable to use a special tool called a "separator inserter." The broad side is used next to the negative plate to loosen the separators so that they can be pushed and pulled at the same time from between the plates (see Fig. 95). In case

FIG. 93.—Removal of the element from the jar.

the separators are not to be used again, a putty knife may be inserted between each separator and the negative plate to loosen them and then they may be pushed from the top and pulled from the bottom until free from the plates.

Separate the positive and negative groups of plates and soak each of them in water for about twenty minutes. They are then ready to be placed away on a shelf if the battery is to be stored.

Pour the electrolyte out of the jar and wash the jar with distilled water.

e. Assembly of a Cell.

To install new separators, place the elements on edge as for removal of separators. Insert the new separator from the bottom. The smooth

FIG. 94.—Draining the element. Five minutes is sufficient and too long a time should be avoided because the negatives may become hot.

FIG. 95.—Use of the separator inserter.

side of the wood separator is to be placed next to the negative plate and the perforated rubber separator between it and the positive plate.

(The Ironclad-Exide battery has only a smooth wood separator between plates.)

Place the element on edge, projecting slightly over the edge of the bench, and place jar over the plates. Then lift the jar and plates in this position (similar to position for draining the element, Fig. 94) to the floor and push element into position. The electrolyte may be in the jar at this time, but it is preferable not to have it so. The inside edge of the jar at the top should be cleaned of compound and wiped with a cloth dampened with dilute ammonia or soda after the element has been inserted as above. It is necessary to have the jar and cover free from all acid, as otherwise the compound will not adhere properly to the surfaces. Care should be taken that no ammonia or soda is allowed to get into the electrolyte.

Before putting on the cover, place the soft rubber gaskets, if used, over the posts. The cover should be replaced while the jar is cold, unless it will not fit readily, in which case warm the outside of the jar with a flame until it becomes flexible enough to allow the cover to fit properly. Care should be taken not to burn the jar. Heat the compound and pour it into position, then trim with a hot putty knife until a level, smooth surface is obtained. Clean off all compound not needed to seal the cover. Replace the cell in the tray in the same position as it was in the beginning.

If there is electrolyte in the cell, first clean the posts with dilute ammonia or soda to neutralize the acid and allow them to become dry before doing anything further.

Trim each post, if a connector puller has been used, until its top is about $\frac{3}{16}$ inch below the top of the connector. This may be best done by means of end-cutting pliers. Clean off the top and sides of the posts thoroughly. A file brush is good for cleaning the top, and gas pliers for cleaning the sides of the posts.

Always have the cover firmly in place and sealed before putting on the connector. If the intercell connector is not of the right length it should be adjusted, and in no case should it be forced into position over the posts, as the jar or cover may be broken on account of undue strains.

f. Lead-burning.

This is a welding process for making a good mechanical and electrical connection between the plates and the strap and between the posts and connector. Burning is done by means of illuminating gas and oxygen, acetylene and air, hydrogen and compressed air, or an electric arc. Illuminating gas and oxygen is the most convenient of the gas methods. The gas is taken from the supply main and the oxygen from

a storage tank. Care must be taken to adjust the burner properly and to prevent explosions. If the tip of the burner becomes stopped, the oxygen will flow into the gas main, owing to its higher pressure, and an explosion may follow. To prevent such an occurrence, a safety device of some sort must be used in the gas main or at each burner. Figure 96 shows a simple device which is in use at a service station for the protection of a number of burners. A similar device is obtainable in the market. The pressure of the oxygen should be about 4 to 5 pounds when used with illuminating gas. The reducing valve on the

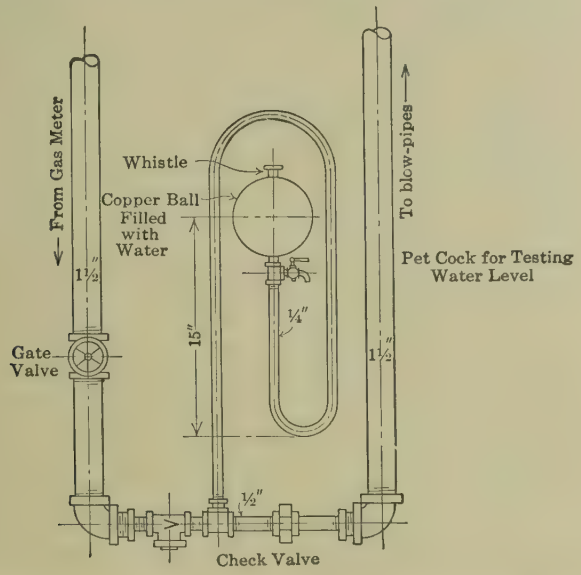


FIG. 96.—Device for protecting the gas main when tip of burner becomes clogged. The oxygen, which is at higher pressure than the gas, cannot flow past the check valve or a flame run back to the meter and cause an explosion.

oxygen tank is usually of the diaphragm type, provided with a gage for indicating the pressure on the outlet side. The design of the valve is such as to maintain a practically constant pressure when a number of burners are being used. The pressure of oxygen is to be set at approximately the right amount by the valve on the tank when the reducing valve is partly open. The fine adjustment of the pressure is then made by opening or closing the reducing valve. Some valves are so constructed that the adjusting screw is to be turned to the right to open the valve or increase the pressure. For this reason it is sometimes thought that the valve is being opened when in reality it is being closed. Use a reducing flame, as it is not desirable to oxidize the lead. Work

with the tip of the inner blue flame and use a rotary motion, working from the center of the post upward and outward. The top of the post should be melted first and then fused to the wall of the hole in the connector; then lead from a piece of burning strip can be run in until the joint is flush with the top of the connector. Finish with a file and file brush. All parts must be thoroughly cleaned of dirt or foreign matter,

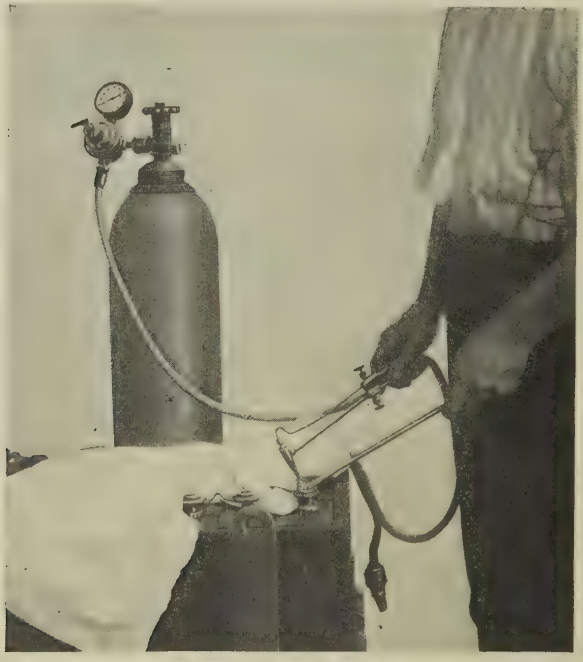


FIG. 97.—Lead burning with a flame of illuminating gas and oxygen. The cells must be blown out, the vent plugs removed and the top of the battery covered with a damp cloth. Oxygen tank should have reducing valve, pressure at burner not exceeding 5 pounds.

as absolute cleanliness is necessary for a successful piece of work. Figure 97 illustrates the burning process above described.

The electric-arc outfit consists of a carbon holder, with connecting cable and clamp and a carbon rod about $\frac{1}{4}$ inch in diameter. The battery on which work is to be done is usually used as a source of current. From two to four cells are required, according to the state of charge. Figure 98 illustrates this method of burning. The clamp is attached to an intercell connector a sufficient number of cells away to give the proper voltage. Care should be taken to have a good connection

between the clamp and connector. The carbon rod should be sharpened to a point and project about 2 inches beyond the clamp. The carbon should be brought to a bright glow by contact with the post which is being worked on. The same process as described for gas is to be followed for making the joint. The carbon should be worked with a rotary motion from the center of the post outward without drawing an arc. The carbon holder should be cooled occasionally by plunging it, with the carbon, into a pail of water. After a time the carbon may fail to work properly, owing to a film of lead oxide, which may be removed by a file or scraping with a knife. It is necessary that the operator use a pair of dark glasses to protect his eyes. If the battery

FIG. 98.—Lead burning with the electric arc. The battery is being used as the source of current, voltage required four to eight volts, operator should wear dark glasses.

is not available as the source of current, a 6-volt "starting" battery may be employed. In this case one terminal is connected to the clamp of the carbon holder and the other to the connection to be burned.

A device for lead-burning called the "pyrotip," operating on alternating current, has recently been put on the market. A small portable transformer reduces the 110-volt circuit to a suitable voltage. The carbon is large in diameter and terminates in a sharp point, which enables the operator to apply the heat at any place that he may desire. The alternating current may be passed through the cell without harm.

9. SOURCES OF TROUBLE

The most frequent sources of trouble in connection with batteries are as follows:

a. Overcharging.

Overcharging produces excessive gassing and this loosens active material in the plates, particularly the positive. This material, sifting down between the separators and the plates, is deposited in the bottom of the jar as a fine brown sediment. Overcharging also increases the temperature of the battery and in some cases may carry it to excessive temperatures which are destructive both to the negative plates and to the separators. Some cases of buckling of the plates are to be attributed to overcharging, although this is by no means the only cause of buckling of the plates. Overcharging, which is accompanied by excessive gassing, results in a needless loss of water, requiring constant attention to keep the cells filled to the proper level with electrolyte. Occasional overcharging is beneficial, but habitual overcharge decreases the period of useful service which the battery can give.

b. Undercharging.

Consistent undercharging of the battery results in a gradual running down of the cells. This is indicated by progressively lower values of the specific gravity readings and a tendency of the plates to become somewhat lighter in color. The sediment deposited in the bottom of the jar when undercharging has been prolonged is usually a fine white powder, consisting principally of lead sulphate. Some of this material is deposited each time the cell is recharged. This effect is not often noticed in batteries of the starting and lighting type. Consistent undercharging generally results in one or more of the cells being exhausted before the others, and in some cases these may become reversed by the other cells of the battery. When this occurs the most obvious remedy is to charge the battery until all the cells are again in normal condition. Insufficient charging is one of the most common causes of buckling of the plates (see Fig. 99). The lead sulphate occupies more space than

Fig. 99.—Buckled plates. There are a number of causes of this, but perhaps the most common is undercharging.

the original material and an excessive amount of it strains the plates.

c. Difficulties with the Charging System.

Difficulties arising in the operation of starting and lighting batteries may in some cases be traced to difficulties with the charging system. The battery is generally held accountable for its own failures and those of the charging system also. Under normal conditions of operation of the car, the battery should begin to charge when a speed of about 12 miles per hour has been reached. Unless the generator cuts in at the proper speed, the battery will not receive its normal amount of charge. There is also the possibility of grounded circuits or partial grounds, which drain the battery and keep it in a more or less discharged condition. This can only be detected by testing the different parts of the circuit with a voltmeter. The charging system is always provided with some means of regulation which prevents the battery from receiving excessive currents when the car is being operated at high speeds, and the regulator should adjust the charging current to the proper value for the ordinary conditions of driving. This regulator may require readjustment to meet unusual conditions of driving or to remedy defects in its original setting. The charging rate should be lower if the car is customarily used for long-distance runs at rapid rates. City driving, on the other hand, requires a higher charging rate for the battery on account of the frequent stops and starts.

d. Corroded Terminals.

Corroded terminals often prevent the battery from delivering sufficient current for starting an automobile engine. This is because the products of the corrosion are non-conducting substances which form a layer between the terminal of the battery and the clamp connector which may be connected to it. This film will not ordinarily interfere with the charging of the batteries or the use of the batteries for lighting lamps on the car, but will make the resistance too great for the passage of the large currents required during the starting period.

e. Cracked or Broken Jars.

Cracked or broken jars of inclosed batteries can ordinarily be detected by leakage of electrolyte through the tray, or, if the crack is slight, by the necessity of periodically adding more water to the cell having a cracked jar than to the others. In such a case, the electrolyte of the

cell will gradually become diluted by the additions of water, and this will result in diminishing the capacity of the cell as well as in the destruction of the wooden box containing the cells. The obvious remedy is to replace the broken jar as soon as it is discovered, and to adjust the specific gravity of the electrolyte in the battery to the proper amount at the conclusion of full charge.

f. Short Circuits.

Short circuits within the cells may be caused by a breakdown of one or more of the separators between the positive and negative plates; by the accumulation of sediment in the bottom of the jars; or, in rare instances, by the formation of a tree-like structure of lead over the tops of the separators from the negative to the positive plates. The evidences of short circuits within the battery are: (*a*) continued low readings of the specific gravity even though the battery is receiving a normal amount of charge; (*b*) rapid loss of capacity after a full charge, and (*c*) low open-circuit voltage. Ordinarily, the open-circuit voltage has little or no significance in determining the condition of the storage battery, but in the case of cells which are internally short-circuited, the open-circuited voltage is nearly always abnormally low and can be taken as evidence of the short circuit. The remedy for this condition is to disassemble the cells, wash out the accumulated sediment in the bottom of the jars, and to replace the old separators with new ones. The sediment in the bottom of the jars conducts metallically, and if enough of it accumulates to touch the bottoms of the plates, a short circuit inevitably develops.

g. Worn-out Plates.

Worn-out plates are ordinarily detected by a marked decrease in the capacity of the battery when it is receiving an adequate amount of charge. If the solution in the cells quickly rises to its proper value when the cells are on charge, but only a small capacity can be obtained on discharge, the battery is worn out. This may be due either to age or poor material used in the construction of the plates. There is no remedy except to replace the plates.

h. Electrolyte Below the Tops of the Plates.

If the electrolyte is allowed to remain consistently below the top of the plates, an abnormal sulphation (see Fig. 100) takes place and the plates crumble. This is generally the result of neglecting to add the

necessary water to replace evaporation. Unless the injurious effects have gone too far, it is sufficient to fill the cells with water to the proper level and allow the battery to continue its normal operation.

Electrolyte should not be added under any circumstances unless it is known that electrolyte has been lost from the cell. Whenever it is necessary to add acid to the cells, the acid should be in diluted form. The cells should be placed on charge and the concentration of the electrolyte within the cells adjusted in the battery before the conclusion of the charge.

FIG. 100.—Negative plate sulphated near the top, showing the effect of too low a level of the electrolyte.

i. Freezing.

Freezing of the electrolyte within the cells will rarely occur in the operation of batteries. In some cases the freezing may be very destructive to the plates, but it is by no means certain that freezing will injure the battery. When freezing occurs, water crystals separate from the body of the electrolyte. These water crystals cause some expansion of the active materials of the plates, particularly if the pores of the plates are clogged with lead sulphate as a result of the discharged condition of the battery. Experiments with small plates in a fully charged condition carried to a temperature below the cryohydric point, so that the entire mass of the electrolyte was solid, showed no destructive action on the plates. Under ordinary circumstances, however, freezing will only occur in the case of batteries which are in a discharged condition, and the results of freezing in such a case may be more deleterious to the plates.

j. Impurities in the Solution.

Impurities in the solution may come from impurities initially present in the sulphuric acid, or in the plates, or they may be added accidentally as, for example, by the use of natural water to replace the evaporation in the cell. Storage batteries are particularly sensitive to certain kinds of impurities, and these have been described in Chapter III. Perhaps

the most common of the metallic impurities found in the storage battery electrolyte is iron. Iron produces discharge of the plates by being oxidized to the ferric condition at the positive plate and reduced to the ferrous condition at the negative plate. During this process the iron diffuses from one plate to the other, but it is not deposited upon either electrode. Unless the amount of impurities present in the electrolyte is serious, they can generally be eliminated by pouring out the electrolyte from all of the cells and flushing them with distilled water, which in turn is also poured out. The cells are then to be filled with pure dilute electrolyte, which is adjusted to the proper specific gravity at the conclusion of a full charge.

With the enormous increase which has taken place in the storage-battery industry as a result of the development of starting and lighting batteries, a number of so-called "patent" electrolytes, containing various ingredients said to be beneficial to the operation of the battery, have appeared on the market. Few, if any, of these have any merit; many are injurious; and the safest rule for satisfactory operation is to keep the electrolyte within the cells as pure as possible.

k. Chipping of the Active Material.

When blocks of the active material break out of the plate, as shown in Fig. 101, the effect may be referred to as chipping. There are a number of possible causes for this effect, which is observed most often with positive plates, but may occur with negatives also. Among these causes are the following: the active material may not have made good contact with the grid; the plate may have been overpasted and the surface blown off by the formation of gas during charge; the active material may have been too hard and have cracked when the plate was dried or after formation; excessive sulphation may have cracked the active material. In most cases the cause of the defect is to be found in the plate itself. The obvious remedy is to replace the defective plates with those of better quality.

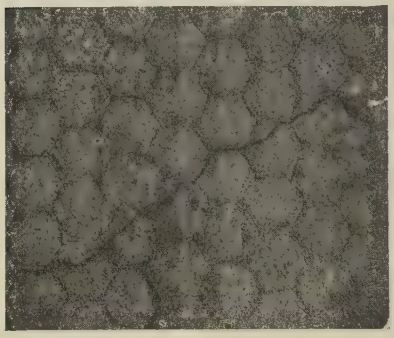
FIG. 101.—Positive plate showing loss of active material as a result of overpasting.

1. Excessive Sulphation.

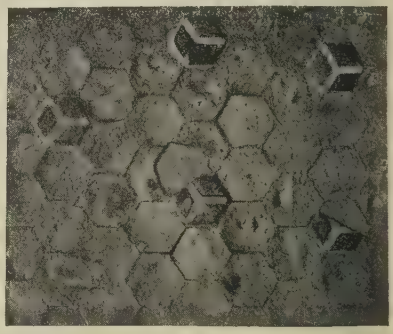
This is generally caused by neglect, or misuse. The sulphation becomes excessive if the acid is too strong or if proper charging is neglected. In Chapter III the relative rates of sulphation of the negative plates in solutions of various concentrations have been given. From these results the reason why electrolyte should not be added to a cell, unless electrolyte has actually been lost from it, is at once apparent. The final specific gravity of the electrolyte after charge is complete depends on the total amount of sulphuric acid in the cell. If all of the lead sulphate in the plates (except a few per cent—1 to 4 per cent—that always remains) has been reduced by charging to sulphuric acid and the specific gravity is still too low, the cell needs acid, but this is of rare occurrence. On the other hand, if acid is added to a cell which already contains the normal amount, two things may happen. First, the rate of sulphation of the negative plates will be increased. This means that the plates will lose their charge faster than normal, by local action. If the battery is in a run-down condition when the electrolyte is added, it may be spurred on to give a little more capacity at the expense of the remaining active material, but the additional capacity obtained will in any case be small and accompanied by the excess formation of sulphate. The pores of the plates become more completely clogged with the sulphate, the active material may be pushed out of the grids, the plates buckled, and the difficulties in charging the plates greatly increased. Secondly, if a battery in this condition is charged fully, the specific gravity of the electrolyte will rise to an abnormally high value, which further accelerates the rate of sulphation of the negative plates and burns the separators. The necessity for adjusting the specific gravity of the electrolyte at the conclusion of an equalizing charge becomes apparent whenever it is necessary to add acid to any cell. Some of the so-called patent electrolytes are merely ordinary solutions of sulphuric acid, harmless enough in themselves; but to pour out the solution of the battery, whatever its state of charge, and add another solution of some other specific gravity will result in diminished capacity if the total amount of acid is too small, or in excessive sulphation if the amount is too great. The latter more generally happens.

The lead sulphate which forms as a result of the reactions that take place during discharge is easily reduced on subsequent charging if too great a time does not elapse. A battery that is allowed to stand in a discharged condition for some time, however, becomes more difficult to charge. The sulphate appears to harden; probably a molecular

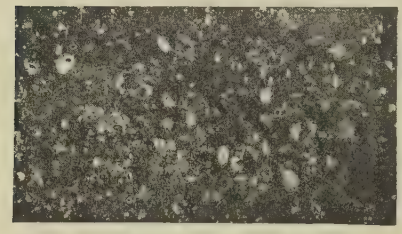
change takes place, but of this there is no very direct evidence. When a battery is in this condition it is said to be "sulphated." Various cures for sulphated batteries have been proposed and some of them have been patented. A simple and effective remedy for this condition is to pour out the electrolyte and fill the cells with water. After being allowed to stand for about an hour, the battery may be put on charge at any rate of current, provided that the voltage at the terminals of



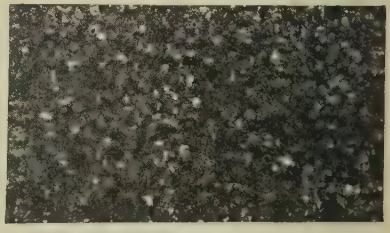
(*a*) Positive, showing a fractured grid.



(*b*) Negative, showing separation of the active material from the grid.



(*c*) Magnified image of sulphate crystals on the positive.



(*d*) Magnified image of sulphate crystals on the negative.

FIG. 102.—Effects of excessive sulphation of plates that were allowed to stand for two years in a discharged condition.

the cells is less than 2.3 volts per cell. It is desirable to make the voltage as near 2.3 volts per cell as is convenient and to give the battery what is practically a constant-potential charge. The resistance of the battery will be high at the start and the current initially small, but the current will increase as the sulphate is broken down. The cells will take the current as fast as they are capable of being charged, and the process becomes more or less automatic, but the temperature must be watched and the batteries cut off or the current decreased if the tem-

perature reaches 40° C. (104° F.). The charging may also be done by the constant-current method. The water which was put in the cells becomes a solution of sulphuric acid as the charge proceeds, and readings of the rising specific gravity can be made. If the final specific gravity obtained after prolonged charging becomes constant at too low a value, more electrolyte should be added. It not infrequently happens that the specific gravity of the electrolyte, initially water, will rise above the normal figure, say 1.300, and this is clear evidence that acid has at some time been added to the cells improperly, that is, when they needed only water.

Ordinarily, the sulphate crystals are so small that they cannot be seen except under a high-power magnification. If they grow slowly for a long time, they may become so large as to be visible to the naked eye. Figure 102 shows sections of positive and negative plates which were allowed to stand in a discharged condition for two years and magnified pictures of the crystals. The crystals on the positive plate were larger than on the negative plate, as shown. This is probably because they grew more slowly. Sections of the active material of the negative plate have been pushed out, the positive active material has pushed up around the edges of the grid, and the grid is fractured.

m. Corrosion of the Grid.

This is an effect noticed with the positive plates, a sample of which is shown in Fig. 103. The trouble starts along the lines of the grid, and lines of sulphation appear. The active material becomes insulated from the grid and cannot be charged. This effect may be caused by the active material shrinking when the paste is dried, if the formula for the paste is not right, or it may be caused by the attack of certain acids present as impurities in the electrolyte. These include nitric, hydrochloric, and acetic acids. Plates in this condition will not give satisfactory service and must be replaced. In aggravated cases, forma-

FIG. 103.—Positive, showing sulphation along the lines of the grid.

tion of the grid ensues. The grid is converted to lead peroxide in part and becomes very brittle, the active material is completely discharged, and the plate falls to pieces. An example of this is shown in Fig. 104.

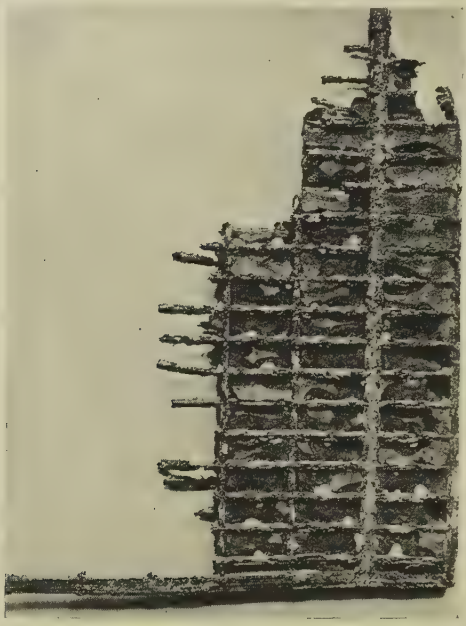


Fig. 104.—Corroded grid of a positive plate, showing the effects of formation of the grid.

n. Reversal.

Reversal may be caused by the overdischarge of a cell deficient in capacity when in series with others that have greater capacity or are more fully charged; generally, however, it is the result of charging a battery in the wrong direction, in which case all cells are reversed. In Fig. 105 is shown a positive plate that has been partly reversed. The reversal became complete along the lines of the grid, but in the middle of each section some of the original brown active material can be seen. The active material has become rough. Sometimes reversal of negative plates of the Planté type is resorted to in order to restore their capacity. The sponge lead of these plates shrinks and solidifies, the plate losing a large part of its capacity. By reversing it to a positive and then again reversing it back to a negative, the capacity can be greatly increased. Reversal of pasted plate cells is not desirable.

o. Growth of Positive Plates.

Planté positives gradually shed active material as they are used, and the formation of additional active material takes place. This is

FIG. 105.—Magnified section of a reversed positive plate. The reversal is complete along the lines of the grid, but in the space between some of the original material may be seen.

made from the underlying lead of the plate. If it takes place irregularly over the surface, growth and buckling result because the lead

FIG. 106.—Planté plates, the positive on the right shows growth and buckling, eight years service.

peroxide occupies more space than the lead from which it is formed. Another cause of growth is said to be the compression to which the lead

sheets are subjected when they are rolled. Plates that have grown several inches in length and a less amount in width are occasionally found. Figure 106 shows a positive plate that has grown and a negative plate, the active material of which has shrunk (see next section). Originally these plates were the same size.

p. Shrinkage of Negatives.

The surface of the negative plate is in a state of flux during charge and discharge, and as a result the sponge lead tends to solidify, that is, to shrink. This results in decreased capacity. To counteract this tend-

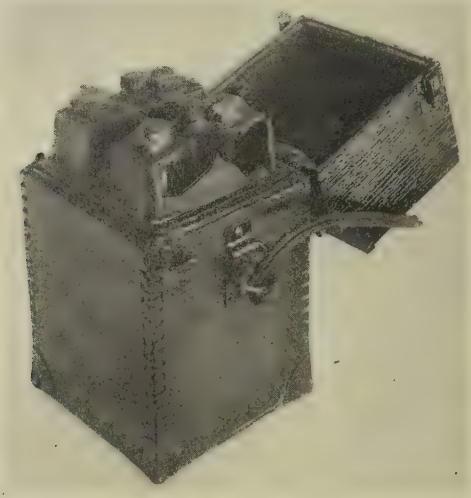


FIG. 107. Storage cells of the double chamber type, damaged by an explosion of gas.

ency, expanders are added to the pastes of the negative plates when they are made as described in Chapter II. The material of Planté plates also shrinks as shown in Fig. 106. Various treatments have been devised to retard this effect, and reversal is sometimes resorted to, as noted in the section on reversal.

q. Explosions.

The gases liberated during charge are hydrogen and oxygen, which explode with violence if a flame or spark ignites them. Figure 107 shows a double-compartment battery which exploded while on charge because of a bad contact. The force of the explosion has blown out the side of the upper compartment and the seams of the carrying case have opened up along the edges.

CHAPTER VII

RESISTANCE

1. RESISTANCE OF THE BATTERY AND ITS RELATION TO THE EXTERNAL CIRCUIT

The internal resistance of a storage cell is very small and for many purposes may be neglected entirely. When large currents are required, however, as when an emergency arises in a central station, or when a tractor begins to pull a heavy load, or in cranking an automobile engine, or when a vehicle is climbing a steep hill, the resistance of the battery and its intercell connections becomes more important. In this chapter is given a simple discussion of the applications of Ohm's law and the resistance characteristics of storage batteries.

Every electrical circuit offers some opposition to the flow of electricity through it. This is called resistance, and the unit of resistance is called the ohm. For any direct-current circuit of which the resistance is constant, the current of electricity which flows is proportional to the voltage applied to it. This relation is expressed by Equation (1) which is called *Ohm's Law*:

$$I = \frac{E}{R}. \quad \ldots\ldots\ldots\ldots \quad (1)$$

The current in amperes is represented by I, the voltage in volts by E, and the resistance in ohms by R.

The current flows through the external circuit from the lead-peroxide plate to the sponge-lead plate, or in the case of the alkaline battery it flows from the nickel-oxide tubes through the external circuit to the pockets containing the iron; that is, the current always flows from the positive to the negative terminal. The current, however, does not begin with one plate and end with another, but flows through the cell as well. The resistance of the circuit is therefore not only the resistance of the external circuit, but includes the so-called internal resistance of the cell or battery. We may therefore write Equation (1) in the following form:

$$I = \frac{E}{R' + b'} \quad \ldots\ldots\ldots \quad (2)$$

where R' is the resistance of the external circuit, b the resistance of the cell, E is the total electromotive force of the cell or, as it is sometimes called, the "open-circuit voltage." The value of b varies somewhat with the state of the charge of the cell and other factors. It is highest when the cell is completely discharged. The current I is the same in all parts of the circuit.

Equation (2) may also be written as

$$E = IR' + Ib. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

That is, the total voltage drop is divided into two parts, one of which is the potential difference or voltage drop, IR', across the terminals of the resistance R' due to the current I flowing through it; the other part is within the cell itself. The quantity b is ordinarily so small in storage batteries that the product Ib may be neglected in comparison with IR'. If, however, the current I is very large, the product of Ib may amount to several tenths of a volt. The effect of this is to reduce the useful voltage of the cell.

The power developed in such a circuit is the rate of expenditure of the electrical energy or, in other words, it is the rate of doing work. The work which the electrical current does is proportional to the current, the voltage, and the time. It is expressed by a unit called the joule or the volt-coulomb, designated by W. If the time in seconds is expressed by t, the work done by the electric current is

$$W = IEt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If the circuit contains resistance only, the energy of the electric current will be converted into heat. By combining Equations (1) and (4)

$$W = I^2Rt = \frac{E^2t}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

That is, the work done in heating the circuit of R ohms is given by Equation (5), from which we may at once obtain the power expended by dividing the equation through by the time, which gives the rate at which the work is done. Letting P represent the total power expressed in watts,

$$P = \frac{W}{t} = IE = I^2R = \frac{E^2}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We may consider the complete circuit as made of two parts as before, one external to the battery and the other the internal resistance of the battery itself. The power expended in each part of this circuit,

considered as of resistance only, is obtained by combining Equations (3) and (6):

$$P = P_1 + P_2 = I^2R' + I^2b = \frac{E^2}{R' + b}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The part I^2b is expended in heating the cell and is lost. It should be noted that this loss increases as the square of the current. This factor reduces, therefore, the watt-efficiency of the battery, particularly at high rates of discharge, and limits the useful power which the battery can give.

When several cells are connected in series the resistance of the battery is the resistance of all the cells added together. If similar cells are connected in multiple, the resistance is reduced by a factor one divided by the number of rows in multiple. Ohm's law applied to a battery having s similar cells in series and p rows in multiple is, therefore:

$$I = \frac{sE}{R' + \frac{sb}{p}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The circuit external to the battery absorbs part of the power which is designated as P, in Equation (7). The voltage drop across the terminals of this part of the circuit will be E' which is less than the total value of E by the amount equal to Ib which is the drop within the cell itself. If the current is I the power expended in this part of the circuit will be

$$P_1 = IE'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If this part of the circuit consists only of resistance, all of the energy will be expended in the form of heat and from Equation (7)

$$IE' = I^2R'.$$

Since the value of E and b are practically constant, the total power generated by the battery in a circuit consisting only of resistance will be small by Equation (7) if the value of I is small, but will increase as the current increases. The maximum current is obtained when the external resistance R' is made equal to zero as shown by Equation (8). In this case the power generated is a maximum, but it is all expended within the battery itself in the form of heat and no useful work is done. Between these two extreme conditions lies the maximum useful power delivered to the external circuit. The total power generated by the

battery, Equation (6), is $P=IE$. The power wasted in the battery (considered as a single cell) is by Equation (7).

$$P_2=I^2b.$$

The power delivered to the external circuit is then

$$P-P_2=P_1=IE-I^2b=\frac{E^2R'}{(R'+b)^2}. \quad . \quad . \quad . \quad . \quad (10)$$

The condition that P_1 shall be a maximum is found by differentiating it with respect to R' and equating to zero;

$$\frac{dP_1}{dR'}=\frac{(R'+b)^2E^2-E^2R'(R'+b)2}{(R'+b)^4}=0$$

whence

$$(R'+b)-2R'=0$$

and

$$R'=b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

That is, assuming E and b to be constant, the resistance of the external circuit which receives maximum power from the battery is equal to the internal resistance of the battery.

The external circuit may contain some apparatus for transforming electrical energy into something besides heat, as, for example, a motor to transform the electrical energy into mechanical energy. In this case

IE' is greater than I^2R'

$$IE'-I^2R'=I(E'-IR')=IE'' \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The factor $(E'-IR')$ is called the counter electromotive force of the circuit. The rate of conversion of energy of the battery into mechanical energy, for given conditions, is equal to the expression $I(E'-IR')$. The useful mechanical energy obtained is equal to this multiplied by the mechanical efficiency of the motor.

The equation for the mechanical power is, therefore, (13) where C_1 is a constant.

$$P_m=C_1IE''. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The counter electromotive force is variable, depending on the speed and the magnetization. The current delivered by the battery is

$$I=\frac{E-E''}{R'+b}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Combining (13) and (14)

$$P_m=\frac{C_1(E-E'')E''}{(R'+b)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

From which the condition for maximum mechanical power is obtained:

$$\frac{dP_m}{dE''}=\frac{C_1(E-2E'')}{(R'+b)}=0$$

whence $E''=\frac{E}{2}$

and

$$P_m=\frac{C_1E^2}{4(R'+b)}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Equation (14) shows that the current delivered by the battery varies inversely as the battery resistance. The battery resistance, therefore, affects the torque and consequently the power which a given motor can exert, since the torque is a function of the armature current according to the equation:

$$\text{torque}=C_2\phi I, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where C_2 is a constant and ϕ the flux.

Similarly, the speed of rotation is given by the equation:

$$\text{speed}=C_3\frac{E''}{\phi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The product of Equations (17) and (18) gives the expression for the mechanical power, Equation (13), in which the constant depends on the units employed.

A battery is seldom required to deliver maximum power, but in emergencies or for short periods of time the relation of battery resistance and voltage to the outside circuit may be important.

Figure 108 shows curves, obtained experimentally, that illustrate the above statements. The battery used for these experiments was a small one, having a capacity of about 140 ampere-hours at the 5-hour rate of discharge. The voltage at the cell terminals falls to one-half its open-circuit value at about 600 amperes. This means that the drop in voltage because of the ohmic resistance of the cell is equal to the voltage drop in the external resistance when the cell discharges 600 amperes. As was shown above mathematically, this is the point of maximum power, and the curve marked " watts per cell " has a maximum at this point. The average internal resistance may be calculated from the slope of the voltage curve. It is found to be 0.0016 ohm. Other cells having different resistances would give results differing from these curves, but the principle is illustrated by this figure.

2. FACTORS WHICH AFFECT THE RESISTANCE

The first and perhaps the most obvious source of resistance in the battery is the electrolyte. Accurate data on the resistance of sulphuric acid solutions are available, and a table of values covering the range of concentrations in storage-battery practice is to be found in Chapter III. Since the resistance of the electrolyte varies with temperature as well as with the concentration, it is not surprising to find that the resistance of a storage cell varies with the temperature. Experiments by Morse and Sargent [1] on the resistance of storage cells have shown

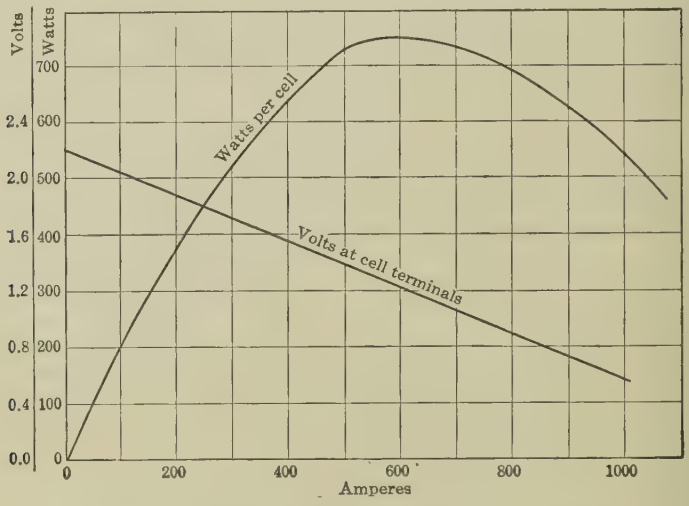


FIG. 108.—Power available at various rates of discharge.

the variation with temperature to be in almost perfect agreement with the temperature-resistance curves for the acid solution of corresponding specific gravity. As the temperature rises the resistance falls.

The presence of the separators adds a small amount to the internal resistance of the cells, particularly if perforated or slotted rubber separators are employed. The resistance of separators cut from various kinds of wood is given on page 48. Some automobile batteries have recently appeared without any separators and accompanied by the statement that all internal resistance, therefore, has been eliminated. This is obviously not the case, and batteries of this type are often a failure.

A third factor contributing to the resistance of the cell is the resist-

[1] Proc. American Acad. Sci., 46, p. 589, 1911.

ance of the active material and grids. The lead peroxide of the positive plates is not a good conductor, and therefore a carefully designed grid is essential. The conductivity of the negative active material is better. Values for the resistivity of the grid material are given in Table II, page 14. The temperature coefficient of metallic conduction, unlike that of the electrolyte, is positive; that is, a rise in temperature is accompanied by a rise in resistance. The resistance due to the electrolyte of the battery is so much larger than the resistance of the metallically conducting material that the positive temperature coefficient of the latter has little effect in neutralizing the negative coefficient of the former.

Another factor affecting the resistance of a storage battery is the state of charge. Lead sulphate, which forms on both positive and negative plates during discharge, is a non-conductor, and its presence materially increases the resistance to the passage of the electric current. The sulphate closes the pores of the plates when they are in a discharged condition and thereby hinders the free access of the electrolyte to the active material. It is evident, therefore, that when the cell is charged the resistance should be less than in the discharged state. This is found to be the case. The resistance of the lead-acid cell begins to increase slowly as soon as the discharge begins, and toward the end of the discharge the increase is much more rapid, reaching values from two to three times as great as the initial resistance. Morse and Sargent have found that the characteristic resistance curves for Planté plates differ somewhat in shape from those of pasted plates. The curves for the Planté plates reach higher values, and the last rapid rise is preceded by a short region of almost constant values which these authors attribute to the distribution of active material on the plate.

During the first part of the charge the internal resistance is high, but it falls gradually until gassing begins, when there may be a temporary rise in values because of polarization phenomena. The resistance may continue to fall for a time after the battery is disconnected from the charging line, because of the gradual equalization of the acid concentration, and the dissipation of the gas layer on the active material.

The resistance of the alkaline batteries also increases during discharge and falls during charge, but the reasons for this are not the same as for the lead battery. The resistance of the alkaline batteries is higher than for the acid batteries of corresponding sizes, mainly because the resistance of the electrolyte is greater.

The resistance of the electrolyte and of the plates is a definite physical quantity independent of the current flowing through the battery. There is another factor opposing the current that is not so

constant or easily defined. It is a resistance at the surface of contact between the electrolyte and the material of the electrode. Newbery [2] has called it the " transfer resistance " and it has the peculiar property that it decreases as the current increases. This effect is particularly noticeable when gas is being liberated at an electrode. Some of the factors which affect over-voltage phenomena affect this transfer resistance also, but the transfer resistance is not the same thing as over-voltage. The transfer resistance has the characteristics of a resistance. It decreases with increasing current, instead of increasing as a back electromotive force or over-voltage commonly does. Theories as to the cause for this effect are conflicting. Chaney [3] investigated the performance of dry cells and concluded that the cause is a surface layer of hydrogen on the anode resulting from local action. Newbery, working with other electrolytic cells, rejected the theory of the hydrogen layer and attributed the cause to a mechanical obstruction of the ions at the transition surface.

During charging there is a back electromotive force that opposes the applied potential. The magnitude of this back electromotive force depends on the concentration of the acid in the pores of the plate and the prevalence of lead ions in the electrolyte. The difference between the impressed voltage and this back electromotive force is the effective electromotive force across the cell and this, together with the resistance, determines the charging current that flows at any instant.

3. METHODS OF MEASURING THE RESISTANCE

The measurement of the resistance of storage batteries presents unusual difficulties, because of the small values and the complications arising at the surface of contact between the electrolyte and the electrodes. Accidental contact resistances at binding posts and elsewhere in the measuring circuit may introduce large errors. The value for any particular cell may vary with the state of charge, the temperature, the current which the cell discharges, and the method of making the measurement. The values obtained by the use of alternating currents do not agree with those from direct-current measurements, apart from any consideration of polarization phenomena.

a. Direct-current Methods.

The numerous direct-current methods which have been proposed for measuring the internal resistance of batteries are based on the

[2] Trans. Faraday Society, 15, p. 126, 1919.

[3] Trans. Am. Electrochem. Soc., 29, p. 183, 1916.

application of Ohm's law. The resistance of a cell is ordinarily defined by the Equation

$$b = \frac{E - E'}{I}. \quad \ldots\ldots\ldots \quad (19)$$

The symbols have the same meaning as in the first part of this chapter. Preece [4] found many years ago that the values obtained by using the above equation vary with the values of I, the resistance becoming greater as the value of I was made smaller. This fact has been found also by many subsequent observers, and it is true for dry cells and other

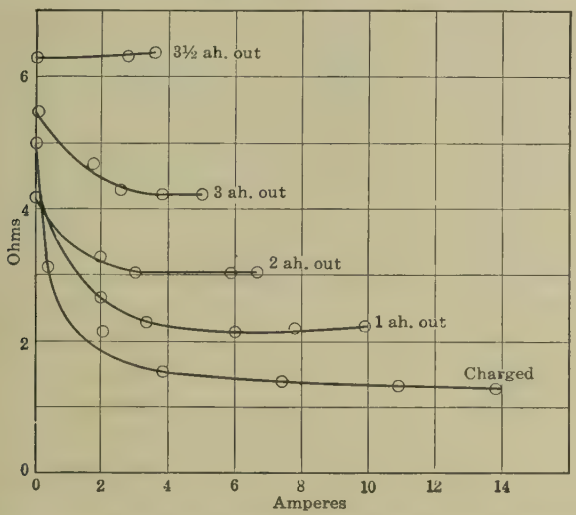


FIG. 109.—Resistance of a 12-cell, three ampere-hour battery at various rates of discharge.

forms of primary batteries as well as storage cells. This effect, which is shown in Fig. 109, is in the opposite direction to that of polzariation and must be ascribed to the transfer resistance at the surface of contact between the plates and the electrolyte. Whatever the cause may be, it is evident that b is not a true ohmic resistance, since it does not obey Ohm's law; but under specified conditions b is an important factor in determining the output of the cell. Northrup [5] states that b can not be called anything more than a quantity which must be added to R to satisfy Equation (2). The name " virtual resistance " has sometimes been applied to this quantity. Notwithstanding the uncertainties that attend the measurement of battery resistance, this quantity is

[4] Electrician, 15, p. 42, 1885.

[5] Methods of Measuring Electrical Resistance, p. 215.

important for both primary and secondary cells. The resistance varies, as is shown in Fig. 109, with the state of charge as well as with the current. A small battery was selected for these experiments as a matter of convenience. The recuperation of a battery after discharge results in a decrease in resistance, as Fig. 110 shows, as well as a gain in voltage.

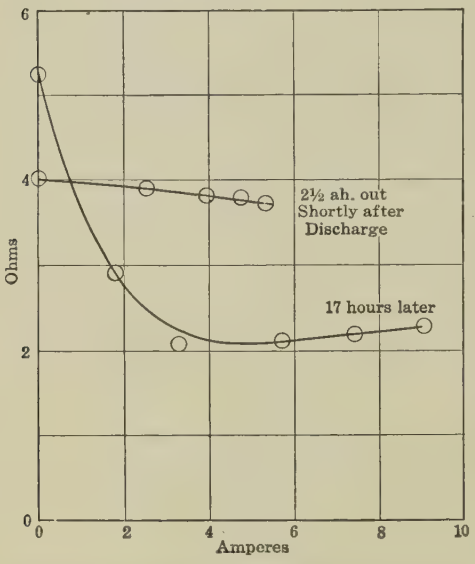


FIG. 110.—Change in resistance during the period of recuperation.

b. Alternating-current Methods.

In view of the difficulties of measuring the resistance of batteries by direct-current methods, the alternating-current methods, of which many have been proposed, deserve careful consideration, but only a few can be described here. It is desirable to prevent the battery from discharging through the bridge. Two methods have been proposed to accomplish this. The first and simplest is to connect two cells of like voltage in opposition and measure the combined resistance of the two. The second method is to put a condenser in series with the cell to be measured.

Nernst and Haagn [6] proposed a method which permitted measurements to be made on one or more cells which might be discharging a direct current through a local non-inductive circuit or be on open circuit as desired. This method was somewhat improved by Dolezalek and Gahl,[7] who eliminated the error introduced by the traveling contact of the bridge wire. The method is as follows:

Two known condensers, C_1 and C_2, are placed in two arms of the bridge. When balanced, the ratio of these condensers determines the ratio of the resistances in the other two arms. One of the resistances can be read directly from the slide wire, and the other, including the battery, can be calculated. If the battery is discharging through the shunt circuit, it is necessary to include in the calculation the value of

[6] Zeit. Phys. Chem., 14, p. 623, 1894.

[7] Zeit. Elektrochem., 7, pp. 429 and 437, 1901.

the shunt resistance. A third condenser is placed in series with the source of alternating current, to prevent the battery from discharging through the circuit. All contacts may be soldered except the traveling contact, but it is apparent that irregularities in this cannot affect the measurement. This method assumes that the battery behaves as a pure resistance in an alternating-current circuit.

The Wien bridge described by Grover,[8] although designed for the measurement of capacity, can be used for the measurement of battery resistance, and it is superior to either of the foregoing bridges. A diagram of this bridge is shown in Fig. 111. The arms are designated as A_1, A_2, A_3, A_4. The condenser C_2 is of known value. The condenser C_1 should be variable to compensate for the capacity of the battery, and must be calibrated. Condensers of good quality are desirable in order that the correction for absorption may be negligible. The resistances R_3 and R_4 are equal, and R_2 is a small fixed resistance. R_1 is a small variable non-inductive resistance whose magnitude will depend on the resistance of the battery and the other resistances in the circuit. The condition for a balance of the bridge is:

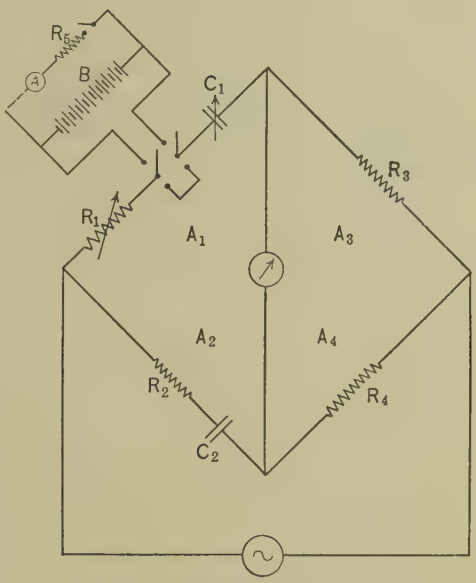


FIG. 111.—Alternating current bridge for measuring resistance of storage cells.

$$A_2A_3 - A_1A_4 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Since the condensers usually have some absorption that may not be negligible, Grover represents the absorption as fictitious resistances ρ_1 and ρ_2, in series with the condensers C_1 and C_2 respectively. Substituting the impedances of the various arms in Equation (20) and separating the real and imaginary parts, two equations are obtained, which are as follows:

$$\frac{\rho_2 + R_2}{\rho_1 + R_1} = \frac{R_4}{R_3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

[8] Bulletin, Bureau of Standards, 3, p. 378, 1907; Sci. Paper No. 64.

and

$$\frac{C_2}{C_1}=\frac{R_3}{R_4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

from which

$$\frac{\rho_2+R_2}{\rho_1+R_1}=\frac{C_1}{C_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Assuming that the quantities ρ_1 and ρ_2 are negligible (if they are not, their values must be determined), R_1 is the only unknown quantity in the equation and its value is obtained from the solution of Equation (23).

$$R_1=\frac{R_2C_2}{C_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

When the battery is in the circuit, the resistance of the arm A_1 is R_1+b and the battery resistance is obtained from the difference of two measurements with the battery in and out of the bridge. The value of C_1 is different in the two measurements. If the battery is discharging through a local circuit of resistance R_5, the effect of this resistance as a shunt circuit must be allowed for in Equation (24).

Another form of bridge suitable for the measurement of battery resistance, devised by the author, may be described as a resonance bridge in which the capacity reactance is balanced by an inductance and the capacity of the battery is calculated from the change in the inductance when the battery is removed from the circuit. This bridge requires a very constant source of alternating current, free from troublesome harmonics. Some special apparatus, such as variable resistances and inductances, is also required.

When a condenser is placed in series with a battery, the impedance of the circuit is given by the expression

$$\sqrt{b^2+\left(\frac{1}{\omega c}\right)^2},$$

where $\frac{1}{\omega c}$ represents the capacity reactance of the condenser and the battery combined. The resistance of the battery, squared, is extremely small as compared with the square of the capacity reactance. In order to eliminate the effect of the capacity, an inductance is tuned into the circuit so that

$$\omega L=\frac{1}{\omega c}.$$

Whence the impedance of the circuit

$$\sqrt{b^2+\left(\omega L-\frac{1}{\omega c}\right)^2}=b.$$

Balances of the bridge should be made with the battery both in and out of the circuit, and this is therefore a substitution method. To

compensate for the battery, a low variable and non-inductive resistance is required. This was supplied by a straight copper wire that could be moved at will into or out of a copper-clad glass tube, filled with mercury. Since the storage cell or any other battery possesses a large electrostatic capacity, the substitution of the mercury resistance for the battery requires a rebalancing of the inductances in the bridge. This was accomplished by the variable inductance, and from the change in this inductance the equivalent electrostatic capacity of the battery may be computed. The cells may be on open circuit while being measured or may be discharging through a local non-inductive circuit at any desired rate. A diagram of the circuit is given in Fig. 112. R_1 and R_2 are non-inductive resistances of small values serving as the ratio arms of the bridge, R_3 is a variable resistance for balancing the bridge, C is the condenser to prevent the battery from discharging through the bridge. L is a variable inductance, B the battery to be measured, with its local circuit consisting of an ammeter and resistance. In place of the battery may be substituted a heavy link. R_4 is a non-inductive variable resistance to be used as a compensating resistance when the link replaces the battery. As a source of the alternating current a 5-watt electron tube, with loose coupling to the bridge, has been used. An amplifier has also been useful at times in the detecting circuit.

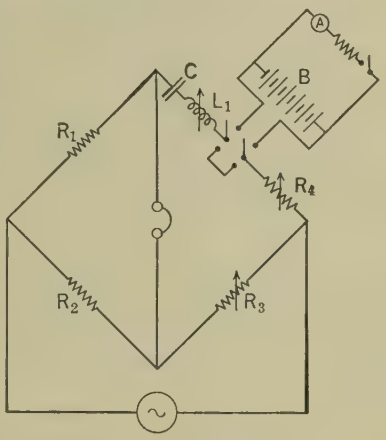


FIG. 112.—Resonance bridge.

Resistances of dry cells measured by such a bridge are constant irrespective of the current and frequency, provided the latter is above 3000 cycles. The values for the resistance were always less than the lowest values obtained by any direct-current measurement. Sufficient data are not at hand to show whether the same is true for storage cells, but it seems likely.

A question naturally arises in view of the above discussion: What is the physical meaning of the resistances as determined by direct- and alternating-current methods, and which is the true resistance? It seems likely that the alternating-current values are the true resistances, but they do not represent the effective values when the battery is being used for direct-current work. The resistance determined by direct-current measurements exceeds the resistance by alternating-

current measurements. Since the transfer resistance varies with the current which flows through the battery, any measurement of resistance, to have a real physical significance, must be made under service conditions. This cannot be easily done in most cases.

TABLE XLVI

COMPARISON OF ALTERNATING- AND DIRECT-CURRENT MEASUREMENTS OF THE RESISTANCE OF A STORAGE BATTERY

Measurements were made on a small battery of 12 cells of about 3 ampere-hour capacity. Values are expressed in ohms.

State of Charge	d. c. Resistance by Oscillograph Method		d. c. Resistance by Voltmeter-Ammeter Method	a. c. Resistance at at 1000 Cycles
	Minimum	Constant		
Charged	1.00	1.08	1.29	0.99
Partly discharged, 2 amp.-hrs.	2.00	2.23	3.2	1.18
Same, after standing 45 hrs.	1.52	1.60	....	1.03
Fully discharged 3½ amp.-hrs.	4.50	5.25	6.4	2.02

A comparison of the alternating- and direct-current measurements of resistance of a small radio " B " battery of 12 cells of the lead-acid type is given in Table XLVI. This shows that the voltmeter-ammeter

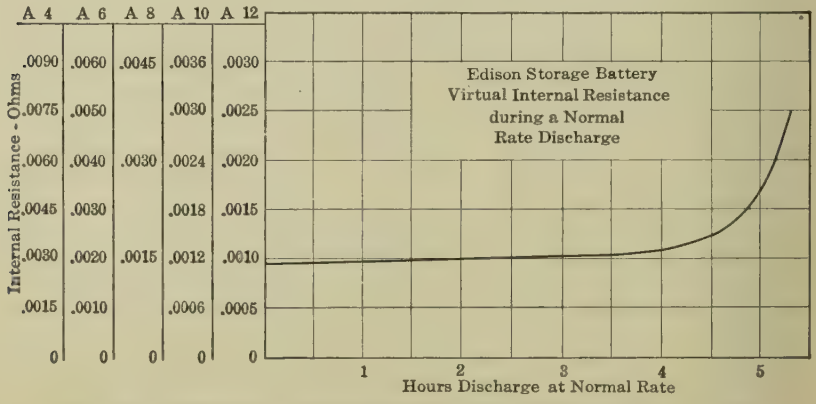


FIG. 113.—Resistance of alkaline storage cells, Edison types A4 to A12.

method is too slow to catch the values obtained by the oscillograph, but probably the voltmeter-ammeter readings come the nearest to representing service conditions. Figure 113 shows the resistance of several sizes of Edison batteries under working conditions.

CHAPTER VIII

EFFICIENCY

The efficiency of storage batteries is defined by the Standardization Rules of the American Institute of Electrical Engineers as follows:

> **10040. Efficiency.**—The ratio of the useful output to the required input. The efficiency from an electrochemical standpoint is the ampere-hour efficiency. It represents the ratio of the quantity of electricity delivered by the battery to the quantity required for a complete recharge expressed in ampere-hours. The energy efficiency is the watt-hour efficiency. It represents the ratio of the energy delivered by the battery to the energy expended in charging it, expressed as watt-hours measured at the terminals of the battery. If the measurements are made at the buses, the watt-hour efficiency of the installation may be obtained. The so-called volt efficiency is the ratio of the average voltage on discharge to the average voltage on charge. The watt-hour efficiency of the battery is customarily taken as the product of the ampere-hour efficiency and the volt efficiency.

This definition distinguishes between the ampere-hour and the watt-hour efficiency, but it is general in its terms since no conditions are specified for either the charge or the discharge. Obviously, the efficiency will vary with the conditions of charge and discharge, and therefore measurements of efficiency should be made in accordance with service conditions. The general expressions for efficiency will be considered first in this chapter, and then the conditions which affect the measurement of both the ampere-hour and watt-hour efficiency.

General Expression for the Efficiency.—If the current discharged by a battery at any moment be designated by I_1 amperes, the quantity of electricity delivered during an infinitesimal amount of time, dt, is $I_1 dt$. For a longer period of time, represented by t_1 hours, the quantity of electricity expressed as ampere-hours is given by the integral:

$$\int_0^{t_1} I_1 dt.$$

Similarly, during the charging period, for which the current at any moment is I_2 and the length of the charge t_2, the total quantity of electricity passing through the battery is

$$\int_0^{t_2} I_2 dt.$$

The ampere-hour efficiency, according to the definition given above, is the ratio of these two integrals:

$$\text{Ampere-hour efficiency} = \frac{\int_0^{t_1} I_1 dt}{\int_0^{t_2} I_2 dt}.$$

If the current is kept constant during both the charge and the discharge, as is usually the case, this expression for the ampere-hour efficiency reduces to the simple ratio:

$$\frac{I_1 t_1}{I_2 t_2}.$$

The power delivered by a battery at any instant during its discharge is the product of the current and the terminal voltage. Expressing the latter in volts by E_1 and the current as above, the power in watts is $I_1 E_1$, and this multiplied by dt is equal to the energy delivered during the element of time. For a discharge lasting for a period of time t_1, the energy in watt-hours is represented by the integral:

$$\int_0^{t_1} I_1 E_1 dt.$$

The corresponding expression for the energy received by the battery during the charging period is

$$\int_0^{t_2} I_2 E_2 dt.$$

The energy efficiency is the ratio of these two integrals:

$$\text{Energy efficiency} = \frac{\int_0^{t_1} I_1 E_1 dt}{\int_0^{t_2} I_2 E_2 dt}.$$

Either the current or the voltage may be kept constant during the charge and discharge. If the current is constant, the expression for the energy efficiency may be written

$$\frac{I_1 \int_0^{t_1} E_1 dt}{I_2 \int_0^{t_2} E_2 dt}.$$

To obtain the integrals $\int_0^{t_1} E_1 dt$ and $\int_0^{t_2} E_2 dt$, the time curves of the

values of E_1 and E_2 are drawn and integrated. The most convenient means of doing this is with a planimeter. Multiplying the first integral by the steady value of the discharge current I_1 and the second by the charging current I_2, the watt-hours delivered and received are obtained.

If both the current and the voltage vary, as when a battery discharges through a fixed resistance, the problem is somewhat more complicated, but can be readily solved.

The current and time factors should be chosen with reference to the conditions of actual service when efficiency tests are to be made.

The Ampere-hour Efficiency.—The ampere-hour efficiency is of importance from the standpoint of the operation of storage batteries, and is a step in the determination of the energy or watt-hour efficiency. The chemical reactions which occur during charging and discharging are reversible, and it is naturally to be expected, therefore, that under favorable conditions the ampere-hour efficiency should be only slightly less than 100 per cent.

The ampere-hour efficiency depends very largely upon the completeness of the recharge. A portion of the charging current is ordinarily wasted in producing gas and this reduces the efficiency. There are also accidental factors which may lower the efficiency, such as (1) the self-discharge of the plates, commonly called local action, (2) leakage of current because of faulty insulation either inside or outside the battery.

Temperature plays an important part in the measurement of efficiency, since the capacity of the battery is dependent very largely on the temperature, as has been shown in Chapter V. Temperatures below normal result in diminished capacity and efficiency, but an increase in temperature may raise the calculated efficiency to over 100 per cent. This does not mean, however, that the battery can continue to furnish more ampere-hours than it receives during charge, as a few repetitions of the experiment would quickly show. The physical significance of a calculated efficiency in excess of 100 per cent is merely that the electrolyte diffuses more readily during discharge because of its decreased viscosity at the higher temperature, and therefore more of the active material of the plates may take part in the reaction than would otherwise be the case. A standard temperature conforming to normal operating conditions should be specified when efficiency tests are to be made.

The rate of the discharge affects the capacity and, to some extent, the efficiency. The higher the rate of the discharge the lower is the delivered capacity, and a smaller number of ampere-hours are conse-

quently required for recharging. The decrease in capacity of a battery because of increased rate of discharge is not accompanied by a corresponding decrease in efficiency. Tests on a group of vehicle batteries discharging at 45 and 90 amperes showed a decrease in ampere-hour capacity of 32 per cent at the higher rate as compared with the lower rate of discharge. Measurements of the ampere-hour efficiency of these batteries at the same rates gave 91 per cent at 45 amperes and 87 per cent at 90 amperes. The decrease in efficiency was only 4 per cent.

The following method for determining the maximum ampere-hour efficiency was suggested to the author by J. L. Woodbridge. A fully charged battery is discharged at some chosen current to a fixed cut-off voltage, careful measurement being made of the exact number of ampere-hours delivered. On the recharge the same number of ampere-hours are put back at the same current. A second discharge is then made to the same cut-off voltage as before. The efficiency of the battery is then calculated as the ratio of the ampere-hours delivered during the second discharge to the ampere-hours put in on the charge. After correcting for the slight increase in temperature as a result of the charge, the ampere-hour efficiency by this method has been found to be within the range 98 to 100 per cent. Such a measurement does not, however, represent the ordinary service conditions.

Nickel-iron batteries gas throughout nearly all the period of charge and are subject to a rather large rate of loss of charge immediately following the charging period. The ampere-hour efficiency is therefore somewhat lower than for the lead-acid batteries. By shortening the charging period, efficiencies of 93 to 95 per cent can be obtained, but the output is then less than normal. The ampere-hour efficiency of a nickel-iron battery may be about 82 per cent under ordinary conditions of operation, but a 7-hour charge following a 5-hour discharge at the same rate would make the efficiency 72 per cent. However, the batteries ordinarily exceed the 5 hours and this improves the efficiency somewhat.

The Watt-hour Efficiency.—The watt-hour, or energy, efficiency is important because it shows the ability of the battery to return the energy which it has received. In this respect it is an important factor in determining the cost of operation. The watt-hour efficiency is affected by the same factors as the ampere-hour efficiency, and in addition to these it is affected by the voltage relations on charge and discharge.

The internal resistance of a battery is small and variable, but it cannot be entirely neglected. Assuming the internal resistance to

have a value b, the decrease of voltage during discharge at a current I_1 is equal to $I_1 b$, and during charge there is a slight increase in voltage at the terminals which is equal to $I_2 b$. The voltage on charge is always greater than the voltage on discharge. The part of this difference which is due to the resistance of the battery is equal to the sum of the two factors $I_1 b + I_2 b$.

By far the greater part of the difference between the voltage of the battery while charging and while discharging is due to polarization. There is some gas polarization, but primarily it is a concentration polarization in the case of the lead battery. The battery behaves as if it contained a very dilute electrolyte when it discharges and a concentrated electrolyte while charging. This is because the electrolyte in the pores of the plates becomes impoverished during the discharge and enriched during the charge. The relation of voltage to the acid concentration has been given on page 166.

The performance curves in Fig. 72 show that the average voltage during discharge at 45 amperes was 1.95 volts per cell and during charge it was 2.28 volts per cell. The ratio of these voltages, which is sometimes called the voltage-efficiency, is $\frac{1.95}{2.28} = 85$ per cent. If the ampere-hour efficiency under such operating conditions could be 100 per cent, the energy efficiency could not exceed 85 per cent. The ampere-hour efficiency at 45 amperes discharge rate was 91 per cent and the energy efficiency was therefore $0.91 \times 0.85 = 0.77$ or 77 per cent. A fair average for the energy efficiency of the lead battery under ordinary operating conditions is about 75 per cent. The watt-hour efficiency of the nickel-iron cells at the normal rate of discharge ranges from 55 to 60 per cent.

It is apparent that the better the equalization of acid within the lead cell, the less difference there will be between the average voltage of charge and discharge. High porosity of the plates and low viscosity of the electrolyte will help to accomplish this.

If the periods of charge and discharge are made very short, the concentration polarization becomes a relatively less important item. Highfield [1] gives the watt-hour efficiency of a central station battery on lighting service during twelve months' operation as 74 per cent, but he reports the efficiency of a line battery on traction service, where the periods of charge and discharge alternated at frequent intervals, as 84 per cent. Hopkinson [2] made a series of experiments in short cycles of charge and discharge. By the time of the cycle he means the sum

[1] Jour. Inst. Elec. Engrs., 30, p. 1070, 1901.

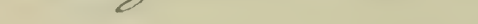
[2] Electrician, 48, p. 211, 1901.

of the time of discharge and the time of charge. Some of his results were as follows:

Time of the Cycle	Energy Efficiency
1 minute	96.5 per cent
10 minutes	93.6 per cent
30 minutes	92.0 per cent

Bailey [3] has gone a step further in this direction and made charges and discharges in cycles as short as $\frac{1}{60}$ second. He obtained energy efficiencies as high as 98.1 per cent. The difference between this and 100 per cent is probably to be attributed almost entirely to losses caused by the ohmic resistance, because the concentration polarization must have been inappreciable at this frequency. Bailey's result is of no importance from an operating standpoint, but it is of very real interest theoretically in showing how perfectly reversible the storage cell is.

[3] Electrical World, 47, p. 829, 1906.



CHAPTER IX

TESTING OF STORAGE BATTERIES

The tests which are of primary importance are those to determine (1) the capacity of a battery at certain rates of discharge; (2) the ability of the battery to retain its charge over a period of time; (3) its ability to withstand vibration (portable types only); (4) the purity of the electrolyte; (5) its period of useful service, or life; and (6) voltage characteristics. The life test requires considerable time and for that reason is not often made. In this chapter is given a general discussion of the tests which apply to various types of batteries. Emphasis is laid on the nature and conditions of the tests, but fixed rules for making them are not prescribed.

1. CAPACITY TESTS

The manufacturer must determine by actual test the number of ampere-hours which any particular size and type of battery, which he makes, can deliver under specified conditions of discharge. From this result he can calculate a conservative ampere-hour rating for similar batteries of other sizes. The purchaser is interested in the capacity because he wishes to know whether the battery in question can deliver sufficient energy to perform the service required of it. It is usually sufficient for his purpose, however, to determine only the ampere-hour capacity. The purchaser is also interested in the capacity as a check upon the manufacturer's rating for the battery.

The ratings made by reliable manufacturers are usually conservative, and their batteries have some margin of excess capacity. Occasional cases have arisen, however, in which batteries have been misbranded, the capacity claimed being so much larger than that which can be delivered as to leave little room for doubt of ignorance or dishonest intent. The willful misrating of storage-battery capacities should fall within the ban on dishonest advertising, but extended and carefully performed tests and calculations are necessary to establish definite evidence of misrating. Some manufacturers have calculated ratings from plate capacities, overlooking the effects produced by changes in

the plate spacing and separator resistance when in assembled batteries. Faults of this kind are easily detected in the tests.

In Chapter V the various factors which affect capacity are discussed in detail. The fundamental points to be observed in making capacity tests of any particular battery are: (*a*) rate of the discharge, (*b*) cut-off voltage, and (*c*) temperature.

a. Rate of Discharge.

As the rate of the discharge is increased, the duration of the discharge is more than proportionally decreased. It is important, therefore, that the current should have a definite and constant value maintained throughout the test, except during intermittent tests. Storage batteries are commonly rated on the continuous discharge, "time" basis; for example, stationary batteries may be stated to have a certain ampere-hour capacity at 8 hours; starting and lighting batteries at 5 hours for the light service and 20 minutes for the heavy service. Such ratings define the test current also. The ampere-hour capacity divided by the time fixes the test current. A stationary battery rated at 4000 ampere-hours for 8 hours is to be tested at 500 amperes. A starting and lighting battery having a rated capacity of 80 ampere-hours at the 5-hour rate and 40 ampere-hours at the 20-minute rate would be tested at 16 amperes and 120 amperes respectively. So it is for any other rating.

A difficulty arises in the testing laboratory when a group of batteries having slightly different ratings is to be tested. It is necessary first to determine whether the batteries are comparable and for the same kind of service. A fair average test current may then be chosen. If the batteries are to be tested in accordance with specifications which state the minimum required capacity, the problem is simplified. For example, if the minimum required capacity at the 5-hour rate is 72 ampere-hours, the test current is $\frac{72}{5} = 14.4$ amperes, although one or more of the batteries may exceed the 5-hour discharge period considerably.

An example of capacity tests for intermittent ratings is found in the case of isolated electric lighting plant batteries for which both intermittent and continuous ratings are provided. The former rating is defined [1] as follows: "The intermittent rating shall be the capacity of the battery when it is discharged intermittently over a period of 72 hours." To avoid uncertainty, because this condition might be met by a variety of tests, a standard test is specified as follows:

[1] Jour. Soc. Auto. Eng., 11, p. 545, 1922.

Discharge at a current rate equal to $\frac{1}{24}$ of the intermittent ampere-hour rating of the battery for an initial period of 4 hours, followed by a 16-hour rest; then discharge at the same rate for two 8-hour periods each, followed by a 16-hour rest, and for a final discharge period of 4 hours.

The rest periods are so arranged as to avoid night work when the test is begun at noon.

b. End Voltage.

The " end " or " cut-off " voltage, as it is preferably called, is the terminal closed-circuit voltage at which it is desirable to stop discharge. Large stationary batteries discharging at normal temperature and the 8-hour or longer rates have a cut-off voltage of 1.75 volts per cell; vehicle and starting and lighting batteries. 1.75 volts at the 5-hour rate, isolated plant batteries 1.75 volts at the 8-hour rate. The cut-off voltages vary somewhat and have not been standardized except by general usage and in some cases by recognized specifications. In the absence of definite specifications, the cut-off voltages are generally determined by the shape of the discharge curve at about the knee of the curve. The capacity which may be obtained beyond this point is small and it is not economical to discharge the battery further.

When discharges are made at higher rates, the cut-off voltages are correspondingly lower. This is because of the increased voltage drop through the cell and the relation of specific gravities of the electrolyte within the plates to that outside. The determining factor in fixing the cut-off voltage is the concentration of acid in the pores of the plate. When proper cut-off voltages are known for two rates, as in the case of starting and lighting batteries, the cut-off voltages for other rates may be found by interpolation. The values for starting and lighting batteries are given by the Motor Transport specifications, as follows:

Rate	Cut-off Voltage
5-hour	1.70
20-minute	1.50

Care must always be taken in measuring these voltages to make the measurements at the cell terminals and avoid losses in leads and intercell connectors.

c. Temperature.

The temperature of a battery under test is ordinarily specified as the initial temperature of the electrolyte, since this is under control of the laboratory. Standard temperatures for most portable batteries are 80° F. or 25° C. (77° F.). The difference is small and may be neglected. The standard temperature for stationary batteries is usually 70° F. The final temperature, which is not under control, is really more important in its effect on capacity. A battery should always be near the standard temperature when a test is made, to avoid large corrections. Corrections may be calculated from Fig. 62 in Chapter V. The temperature correction varies with the rate of the discharge, as shown in Fig. 63.

d. Accuracy.

The accuracy of the measurements made in any determination of capacity deserves especial mention. To attain a satisfactory accuracy of 3 per cent or better, the current must be held constant to within close limits by regulation. Hand-operated rheostats are suitable for regulation if the steps are small, but carbon resistances afford the best means for continuous regulation. The ammeter chosen for the test should have a scale permitting readings to be made directly to 1 or 2 per cent of the test current, and it should be calibrated. The time is easily measured to 1 per cent, except in the case of high-rate discharges such as the 20-minute rate for automobile batteries or the 5-minute rate for aeroplane batteries, for which especial precautions must be taken.

When the end of the discharge is approaching and the knee of the voltage curve is reached, the voltage may change so rapidly as to make it difficult to maintain the current constant at the time when it is most important to do so. To overcome this difficulty, recourse may be had to the use of " booster batteries." The battery under test is connected in series with a battery of larger capacity which serves to maintain the current and decrease the percentage change in voltage in the circuit. For example, if the drop in voltage of the test battery is 0.2 volt per cell, or 10 per cent of the voltage of the cell, the use of nine booster cells in series with this will reduce the voltage fluctuation to 1 per cent, provided the latter are of sufficient capacity. The proper number of booster cells to be used during test is determined mainly by convenience; even a few are of assistance, and ordinarily the ratio would not be as high as 9 to 1.

Careful and systematic records throughout the measurement of capacity are important. The records should include the following: date of previous charge, date of the discharge, number of the cycle, initial specific gravity and temperature of each cell, initial open-circuit voltage of each cell, closed-circuit voltages at appropriate intervals with record of the time in each case (the intervals being shorter as the end of the experiment is approached), the cut-off voltage for the battery and the exact time that it is reached, final specific gravities and temperatures for each cell. It is often worth while to repeat the final specific gravity and temperature measurements after several hours because equalization of the specific gravity of the electrolyte within the pores of the plate with that outside takes place slowly.

Since the capacity of new storage cells increases rather rapidly from one cycle to another, it is necessary that a new battery be given several preliminary cycles of charge and discharge before determining the capacity. Four cycles are usually enough, but more are preferable. The capacity at any particular rate is influenced by the previous discharges (p. 205), and therefore when changing to a different rate of discharge a preliminary cycle at the new rate should precede the measured experiment. In testing any battery it is desirable to determine the capacity at several rates of discharge, although the final judgment of its performance may be based on the results at the normal rate.

e. Causes of Failure.

Batteries which fail to meet capacity tests often require special attention, since it is always desirable for a testing laboratory to report the cause of failure as well as the fact. Experience is the best guide, but if the observations have been carefully made, an analysis of them may suggest the cause of failure. The following items are suggested as a guide to the general procedure:

(1) Compare the open-circuit voltages before discharge with Table XXXI. Appreciably low values may indicate internal discharge due to short circuits through a split separator, excessive sediment, or similar cause.

(2) Examine voltage readings throughout run and see if they progress regularly except for the "*coup de fouet*" (see p. 229) at the start. Erratic readings may be an indication of bad contacts, loosely burned plates, internal short circuits. In case of 2-volt changes occasionally observed, the reversal of one cell is indicated.

(3) Examine the gravity readings to see whether the range is normal for the type of cell under test. If the range is too small, and the plates are in good condition, the indication is that the electrolyte does not circulate freely. Causes for this are high-resistance separators, separators without corrugations, wrong side of separator next to positive plate, or the addition to the electrolyte of some foreign substance which increases the viscosity. If the gravity range is abnormally great, the amount of electrolyte may be too small. Estimate the total amount of electrolyte if possible, and make use of Table XV, which will show the possible output for the amount and range.

(4) The capacity of the cell is usually limited by the positive plate, but in some cases the negative plate may be deficient. The plate capacities can be determined by the use of the cadmium electrode (see p. 212) which will indicate whether either plate is deficient.

(5) By dismantling the cell or battery, and examining the plates and structural details, defects arising from poor manufacture or abuse are often revealed. Chemical tests of the electrolyte may reveal impurities that produce excessive local action.

Figure 114 shows a rack for testing storage batteries of the starting and lighting and portable types. It is arranged in six sections, each accommodating four batteries. Each section is arranged with resistances to be used for regulating both charge and discharge, and switches are provided which permit any battery to be cut in or out of the circuit when necessary without interrupting the operation of the others.

2. TEST FOR THE RETENTION OF CHARGE

Besides determining the capacity of a battery, it is desirable to determine its ability to retain the charge over a considerable period of time. The Motor Transport Division's specifications for automobile batteries specify that a battery must not lose more than 30 per cent of its capacity during a standing period of four weeks. This is an average loss of about 1 per cent per day. The test is made as follows: After a careful determination of the capacity at the 5-hour rate, as outlined in the preceding section, the battery is fully charged and allowed to stand on open circuit at room temperature for a period of four weeks, following

which it is discharged under the same conditions as before and the percentage loss in capacity computed as the ratio of the decrease in ampere-hours delivered to the original capacity in ampere-hours.

The loss in capacity will depend on the specific gravity of the electrolyte, the temperature, and the purity of the electrolyte. The amount of the loss allowed by the specifications is liberal and should cover any battery of reliable quality containing electrolyte not exceeding 1.300 in specific gravity. Lower specific gravities should result in smaller losses. On test of seventeen different makes of batteries, the

FIG. 114.—Rack in use at the Bureau of Standards for testing small types of storage batteries.

smallest loss observed was 4 per cent and the largest 85 per cent; the average of the batteries which complied with the specification was 13 per cent.

One reason for the relatively small loss in capacity in some cases is the fact that the negative plates at which the greatest local action occurs usually exceed the capacity of the positives by a large amount, and it is possible in such cases, therefore, for them to be considerably affected without materially changing the battery capacity. A continuation of the test for an additional period may or may not show

greater losses, because of the available capacity of the negatives falling below that of the positives. The actual rate of the local action at the negatives decreases as the specific gravity is lowered (see Table XIX). Positive plates of the Planté type usually suffer more from local action than pasted positives.

The causes for loss in capacity while standing idle are local action and internal short circuits. The normal rate of local action is shown in Tables XIX and XX of Chapter III. Local action is accelerated by the presence of certain impurities in the electrolyte. Of these, iron is the most common and the most easily eliminated by pouring out the electrolyte. Platinum, although rarely found, is exceedingly destructive even in amounts of only one part in 10,000,000. Manganese, copper, and the presence of chlorides, nitrates and acetates are also sources of trouble. Among the causes of internal short circuits are excessive sediment, defective separators, metallic particles falling into the cells through the vents and, in rare cases, porous sealing compound. Stationary batteries, if not properly cared for, may also lose charge because of poor insulation.

3. VIBRATION TEST

This test applies particularly to automobile and aeroplane batteries, but may be used with other portable types to develop possible defects in lead-burning, sealing of terminal posts, vent-plug design, and shedding of active material.

Figure 115 shows a vibration board driven by a cam on a motor at the left. The board vibrates in a simple harmonic motion of 5 millimeters' displacement (battery position) with a frequency of 1000 cycles per minute. Any departure from a simple harmonic motion changes the maximum acceleration value and modifies the test. For this reason a short connecting rod cannot be used. This vibration board has been in use at the Bureau of Standards for several years, and similar apparatus has been adopted by several manufacturing companies.

The battery is fastened to the vibrating board by hold-down clamps and vibrated for one hour, during which time it is discharging at any convenient rate (5-hour rate generally used). It must maintain a steady voltage and current during this time. Fluctuations are generally due to plates breaking loose from the straps, as may happen if the lead-burning is not properly done. Failure occurs most commonly at the terminal posts, which may become loose and allow the electrolyte to flood the top of the battery; vent plugs, if not provided with baffle plates, will usually allow electrolyte to escape. Excessive sediment

may be produced, and cells may become loose in the tray. A battery of good design and workmanship should pass this test without difficulty. At the conclusion of the tests the cells are examined for broken plates, connectors, straps, and sediment in the bottom of the battery jars. It is not necessary to test the batteries to destruction, but it often happens that poorly constructed batteries will fail in a very few minutes. Batteries of satisfactory construction, however, may last for five hours

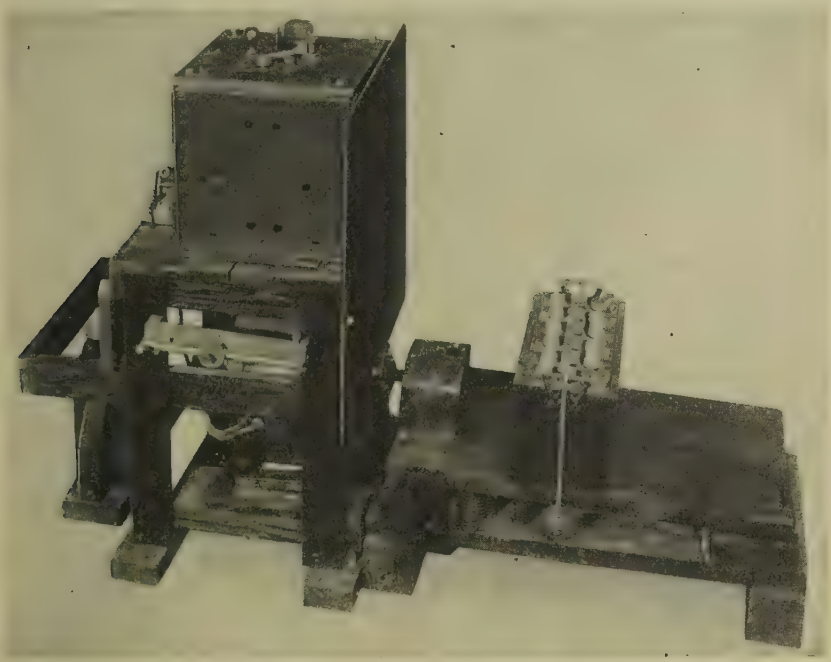


FIG. 115.—Vibrating board for testing automobile and aeroplane batteries.

or more if the test is continued that long. One hour was chosen as an arbitrary figure, the successful completion of which indicated that the battery was of satisfactory construction.

This test is considered superior to a bumping test, because the batteries in service are subjected to vibrations; also the test is easily specified in simple mathematical terms.

4. TESTS FOR PURITY OF THE ELECTROLYTE

Tests for the purity of the electrolyte form an important part of the complete test of a storage battery, but cannot be made satisfactorily when suitable chemical laboratory facilities are lacking.

The presence of some of the impurities can be readily determined by inspection of the cells. Platinum causes excessive gassing of the negative plates. This may be observed when the cells are on open circuit, if the cells are contained in glass jars, or a sample of the negative plates may be removed and placed in a beaker containing a solution of pure sulphuric acid. It is to be observed, however, that gassing will be somewhat in evidence even in a normal battery, particularly after the termination of a charging period. Negative plates which are contaminated with platinum will continue to gas until they are completely discharged. When manganese salts are present in the electrolyte they may ordinarily be detected by the characteristic permanganate color which appears at the positive plates when the cells are on charge. Hydrochloric acid, nitric acid, and acetic acid, if present in any considerable amount, may be detected when the cells are on charge by the characteristic odors of chlorine, nitrous oxide, and acetic acid, respectively.

Chemical methods for the detection of impurities in storage-battery electrolytes follow more or less the general procedure for analytical determinations, but they present the special difficulty that the impurities are present normally in small amounts in a fairly concentrated solution of a strong mineral acid. The methods which are described in the literature for the testing of storage-battery electrolytes are for the most part qualitative tests. It is desirable that such tests should be made quantitative determinations in order to determine the compliance of the electrolytes under test with generally recognized specifications for the degree of purity required. The quantitative methods are mostly colorimetric tests in which comparisons of the samples under test are made with standard solutions of sulphuric acid or with the electrolyte from storage batteries which has been treated similarly. In this work a sharp distinction must be drawn between used and unused solutions. When tests are being made of sulphuric acid solutions that have not been used in storage batteries, they should be compared with standard samples of unused sulphuric acid of a known degree of purity. On the other hand, when the electrolyte is taken from storage cells, comparison must be made with standard samples of pure electrolyte withdrawn from storage cells in actual use. When a considerable amount of testing of this character is to be done, it is convenient to prepare the used electrolyte by withdrawing it from a battery of good quality and replacing the electrolyte so drawn by fresh electrolyte of the same specific gravity, repeating the process after several cycles of charge and discharge until a sufficient quantity of the used electrolyte has been accumulated for the chemical tests.

The choice of the methods for the detection of impurities in storage-battery solutions depends, first, upon the possibility of making the determinations quantitative, second, upon the accuracy which can be obtained by the method, and third, upon the presence or absence of certain impurities which may interfere with the results of the test. In order to determine the presence or absence of these impurities, preliminary tests are sometimes desirable before deciding upon the method of test to be used for the quantitative detection of any particular impurity. The accuracy which can be obtained will depend very largely on the care with which the reagents are prepared and the preparation of the colorimetric standards for comparison. It is not possible within the scope of this treatise to give in detail the considerable number of tests which are used for the determination of the various impurities and the conditions under which any one test is to be preferred to others.

The sensitiveness of the usual tests under the best conditions is as follows: The sulphocyanate test for iron may be made so sensitive as to reveal the presence of one part in 50,000,000 of iron in the solution. A distillation method with the use of Nessler's reagent may be made to show one part in 20,000,000 of ammonia in the solution. The potassium iodide method is commonly employed for the detection of platinum and has a sensitiveness of one part in 2,000,000. For the detection of nitrates, brucine is used, the sensitivity being one part in 2,000,000. Ferrous sulphate is a more certain indicator for nitrates, although less sensitive than brucine. The brucine test may be affected by charging the cell. Sodium bismuthate is used for the detection of manganese and will reveal the presence of one part in 2,000,000. Nitrites may be determined in as small an amount as one part in 1,000,000, by the use of dimethylaniline. Copper is determined to a similar accuracy by the use of potassium ferrocyanide. Chlorine may be determined by the use of silver nitrate to one part in 1,000,000, but in used electrolyte silver nitrate will not show total chlorine as it will not react with the perchloric acid. Antimony and arsenic may also be determined to about one part in 1,000,000 by the use of hydrogen sulphide under increased pressure. The presence of calcium in the electrolyte is determined by the use of ammonium oxalate, the sensitiveness being about one part in 50,000. These are by no means all of the tests used for the determination of these substances, but they are the tests which would naturally be chosen provided their use is not prevented by the presence of other impurities which interfere with the reactions. When any of the impurities are present in relatively large amounts the colorimetric comparisons become difficult and the accuracy of the methods is considerably decreased.

The determination of nitrates and nitrites has been investigated at the Bureau of Standards by L. B. Sefton. More than fifty methods for the determination of these substances have been described in the chemical literature, but only those which were found suitable and reliable for battery purposes were selected for final study. Nitrates cannot be estimated in the presence of nitrites, but nitrites can be estimated in the presence of nitrates. When iron is present in the electrolyte the brucine test under some restrictions, was found reliable for the determination of nitrates and nitrites, and the dimethylaniline test was found to be the best for the determination of nitrites. The results of this investigation have been published as Technologic Paper No. 149 of the Bureau of Standards.

No satisfactory simple quantitative method has been devised for the determination of acetic and similar acids in the electrolyte. The test for acetic acid mentioned by Kretzschmar [2] is based on the odor of the cacodyl reaction.

Aside from the chemical tests for the purity of the electrolyte, it is possible to determine the presence of impurities of the electronegative metals by spectroanalysis of material removed from the surface of negative plates. This method has been applied particularly for the detection of small amounts of platinum, since it is possible to effect a concentration of the impurity, even when present in very small amounts, by scraping the surface of the negative plates. A quantitative estimate of the amount of impurities can in some cases be made from the relative intensities of the spectrum lines.

Such impurities as platinum and other metals which deposit on the negative plates can seldom if ever be detected in electrolyte drawn from the cells, since these impurities are left behind on the plates.

5. OTHER TESTS

a. Low-temperature Tests.

Because of the use of storage batteries on automobiles in cold climates and on aeroplanes at high altitudes, the low-temperature tests are often of great importance. The low temperature does not materially lower the open-circuit voltage of the cells (see p. 163); but it does increase the resistivity of the electrolyte, which lowers the available voltage at the terminals during discharge; and it increases the viscosity of the electrolyte and thereby reduces the available capacity. No temperature has been standardized for these low-temperature tests,

[2] Die Krankheiten des stationären elektrischen Blei-Akkumulators, p. 110.

but a number of tests have been made at 10° F., which is recommended as a good average condition. The charging characteristics also are different at low temperatures. The maximum voltage at the end of charge may be materially higher.

b. Five-second Voltage Test.

Starting and lighting batteries are sometimes given a 5-second voltage test at high rates of discharge, to obtain data for the design of starting motors and for selecting the proper size of battery for any given installation. The test consists in determining the voltage at the battery terminals at the end of 5 seconds of continuous discharge at a number of different rates within the range of 10 to 1200 amperes, at 80° F. and 10° F. This is not a desirable test for judging competitive makes, because it gives the advantage to the batteries of lowest resistance, which may contain soft separators and thin plates.

c. Test for Temperature Rise.

This test is designed to determine the rise in temperature of the electrolytes when overcharged at various rates. From the data thus obtained the proper charging rate can be calculated. This test is of little interest except to the manufacturers of batteries and starter systems.

d. Life Test.

This is one of the most important tests, but is seldom made because of the time and expense involved. Data on the useful life of the large stationary batteries, train lighting, and some truck and vehicle batteries may be obtained from actual installations of these batteries. In such cases it is necessary that they receive proper care and that systematic records of performance be kept. A life test made in a laboratory may lead to incorrect results unless details of the charge and discharge are carefully worked out to simulate the working conditions; for example, charge at constant potential is usually less destructive than charge by constant current. Two cycles is about the maximum that can be accomplished in 24 hours without excessive rise in temperatures. Some batteries are incapable of more than one cycle.

No general agreement has been reached as to a definition of the life test; but within the past few years it has become the custom of a number of the manufacturers of starting and lighting batteries to make a so-called life test by keeping the battery on continuous charge at 80

per cent of its normal rate of discharge. Periodic determinations of the capacity are made to determine the condition of the battery. Such tests may be made every ten days or two weeks. A continuous charge at this rate results in hard and almost continuous gassing of the cells. It is necessary to add water to them, therefore, at frequent intervals. With this condition of test, destruction of the separators usually begins in the course of about six weeks, and the complete breakdown of the cells is accomplished within a few months. This is, of course, much shorter than the useful life of the battery under ordinary conditions of service. Comparative tests made by this method on different kinds of batteries afford, however, rather questionable information as to the relative abilities of the batteries to withstand service conditions.

e. Efficiency Tests.

The measurement of battery efficiencies has been discussed at length in Chapter VIII, and little remains to be said about it at this place. Efficiency tests are of secondary importance, and quite often the results are an indication of the efficiency of the experimenter as well as that of the battery.

The ampere-hour efficiency is calculated as the ratio of the ampere-hours output of the battery to the ampere-hours put in during charge. The conditions of charge and discharge should be carefully chosen and adhered to in all the tests. Since the charging current, besides restoring the active materials of the plates, may produce gassing, the efficiency will be lowered in proportion as the quantity of gas produced is increased. By eliminating gassing altogether and correcting for temperature, it is possible to show that the current efficiency very closely approaches 100 per cent. This is seldom the normal condition of operation, however, as some gassing almost inevitably occurs. In making an efficiency test, therefore, it is necessary that the operating conditions be clearly defined. The chief factors affecting the current efficiency are gassing, temperature variation, and the rates at which the battery has previously been discharged (see p. 305). Preliminary discharges, at the rate which is to be used for the final test, should be always made.

The watt-hour or energy efficiency is of greater importance than the current efficiency because it is an important factor in computing the cost of operation of a battery. The watt-hour efficiency is equal to the ampere-hour efficiency multiplied by the ratio of the average voltage during discharge to the average voltage during charge. This ratio is sometimes called the "voltage efficiency." The average voltage is obtained from the time integral of the voltage curve. The most convenient method of obtaining this is by the use of a planimeter. If

integrating watt-hour meters of suitable range are available, the ratio of the watt-hours of charge and discharge may be obtained directly and the energy efficiency calculated without the necessity of measuring the ampere-hour and voltage efficiencies.

The watt-hour efficiency is affected by the same factors as the ampere-hour efficiency, and in addition by the factors that affect the voltage, viz.: polarization, internal resistance and, to a small extent, temperature. To get a high energy efficiency it is necessary to avoid gassing as far as possible and to maintain the smallest possible difference between the average voltage of charge and discharge. The latter condition necessitates low internal resistance, abundance of electrolyte, and maximum porosity of the plates.

f. Tests of Intercell Connectors.

In the case of batteries intended for discharges at high rates, the resistance of the intercell connectors becomes important. In Chapter X (p. 352) is given a table showing the power losses in the intercell connectors of batteries of the vehicle type. A test has been provided in the specifications of the Motor Transport Division of the War Department for intercell connectors on starting and lighting batteries. This test is specified as follows:

> " The voltage drop in the intercell connectors is not to exceed 10 millivolts per inch of distance between post centers, when discharging at the 20-minute rate."

The test is made by " stabbing " the post centers with sharp metallic points connected to a suitable millivoltmeter through flexible leads, when the current flowing from the battery is adjusted to the required value.

g. Tests of Jar Material.

Standard sizes of jars, so far as they have been adopted for the various types of batteries, are listed in Chapter X as part of the description of the batteries. Some tests to determine the quality of rubber and glass jars have been adopted as standards, and these are described here.

Starting and Lighting Batteries.—The standardization of hard rubber storage-battery jars for starting and lighting batteries on passenger automobiles, adopted August 27, 1918, calls for material having a tensile strength of 3000 pounds per square inch and an elongation

(before rupture) of 5 per cent. Rejection limits were specified as follows:

Tensile strength less than

3600	lbs. per	square	inch with	elongation less than	3 per cent
3300	"	"	"	"	4 "
3000	"	"	"	"	5 "
2700	"	"	"	"	6 "

The test specimens (without seams) are cut as shown in Fig. 116. Some uncertainty in interpreting intermediate values has arisen, but this may be avoided by plotting elongation against tensile strength. The sector of accepted values lies above this line and between the

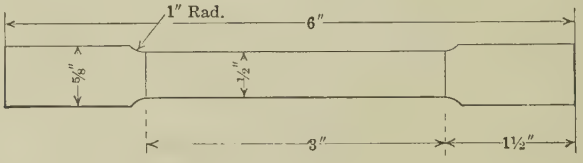


Fig. 116.—Test specimen of the jar material.

abscissa 2700 and the ordinate 3 per cent. Since these specifications were prepared, several excellent jars, of slightly smaller tensile strength but much greater elongation, have appeared on the market. High elongation is to be preferred if accompanied by a reasonable tensile strength.

An electrical breakdown test was also specified for the testing of individual jars, as follows:

> " If the jar, when momentarily subjected on all parts of its surface to a voltage of 18,000 volts a.c. when supplied by a transformer of not less than ½ KW. capacity, is perforated or burned through any defect, either of material or workmanship, jar will be rejected."

Vehicle Battery Jars.—The Society of Automotive Engineers has standardized jars of this type. Two different qualities of the hard rubber material are permitted under these specifications. Jars intended for use on electric passenger vehicles correspond in quality to jars for starting and lighting batteries. Batteries for commercial vehicles receive harder service and are subject to more severe requirements. For the latter a nominal tensile strength of 5000 pounds per square

inch, with an elongation of 6 per cent, is specified. For values differing from these, the product of the tensile strength and elongation is required to be not less than 30,000.

Glass Jars for Railway Signal Batteries.—Specifications for quality of glass storage-battery jars have been adopted by the Signal Section of the American Railway Association These relate primarily to the ability of the jars to resist temperature changes without cracking.

CHAPTER X

PRESENT-DAY USES FOR STORAGE BATTERIES

1. STARTING AND LIGHTING BATTERIES

a. Development of Starting and Lighting Systems.

One of the most notable developments in storage batteries has been the application of them to starting and lighting service on automobiles and trucks. Starter systems for internal-combustion engines were first suggested about 1902, but the development of the electric systems began about 1911. Between 1912 and 1915 a number of different systems were devised, and electric starters for automobiles became almost universal. Before the electrical systems were developed, a number of devices of other kinds were tried. These included various compressed air, acetylene, and mechanical starting devices which have now been superseded by the electrical system. Aside from the fact that many of these earlier starting devices were not entirely satisfactory, the demand for electric lights on automobiles was an important factor in establishing the supremacy of the electric starting systems.

The development of small storage batteries, having relatively large capacity and capable of delivering current at a high rate of discharge, was made possible by the use of pasted plates and thin separators. In the course of the early experiments, it was found that storage batteries could be discharged at rates much greater than the so-called normal rate without doing injury to the battery, and that the batteries could be charged by small generators attached to gasoline engines and driven by them. From small beginnings in 1911, the industry has grown to the point where there are approximately 10,000,000 automobiles electrically equipped with starting and lighting devices in use at the present time.

b. Principal Parts of Starting and Lighting System.

The principal parts of the starting and lighting system of an automobile include the motor, which cranks the engine; the generator, which supplies current when the car is running; and the battery, which serves

as a reservoir of power for cranking the motor, for lights, and for ignition also when the generator is not running or is below the cut-in speed. The starting and lighting systems are commonly classified as single-unit and two-unit systems. In the former, the motor and the generator are combined. During the cranking period this motor-generator operates as a relatively low-speed motor and cranks the engine; after the engine has started, it functions as a generator. Such a system is shown in the diagram in Fig. 117. Two-unit systems, on the other hand, consist of separate motors and generators. Such motors run at much higher speeds and are consequently smaller in size. They are auto-

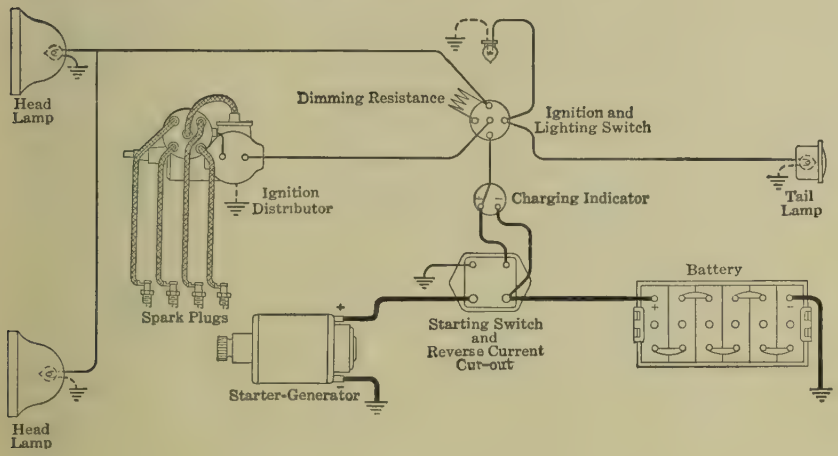


FIG. 117.—Diagram of a single-unit starting system.

matically disconnected from the engine after it has started, and the generator, which is usually driven by the pump shaft, automatically begins to charge the battery when the engine has attained a certain predetermined speed. Such a system is shown in Fig. 118.

The batteries for starting and lighting systems are for the most part of 3 or 6 cells, giving 6 and 12 volts respectively. In the early development of electric starting systems, much higher voltages were used, 30, 24 and 18 volts being common. These higher voltages have now been superseded by the 6- and 12-volt systems. The 6-volt system predominates over the 12-volt system in this country, but 12-volt systems are commonly used on European cars. One factor which has undoubtedly been important in developing the 6-volt systems has been the fact that 6 volts were commonly used for the ignition and 6-volt lamps were the first standard miniature lamps.

c. Description of Starting and Lighting Batteries.

Types and Sizes.—Starting and lighting batteries consisting of 3 or 6 cells are made in a great variety of sizes. In some cases, battery manufacturing companies have been making as many as 150 different sizes of the so-called master batteries, to which further variations are given by adding terminals of various types to accommodate any particular make or model of car. The large number of sizes of batteries of this type has been the natural outcome of the individual ideas of automobile manufacturers. Too often the battery has been made to fit any space that might be available on the car. Standardization

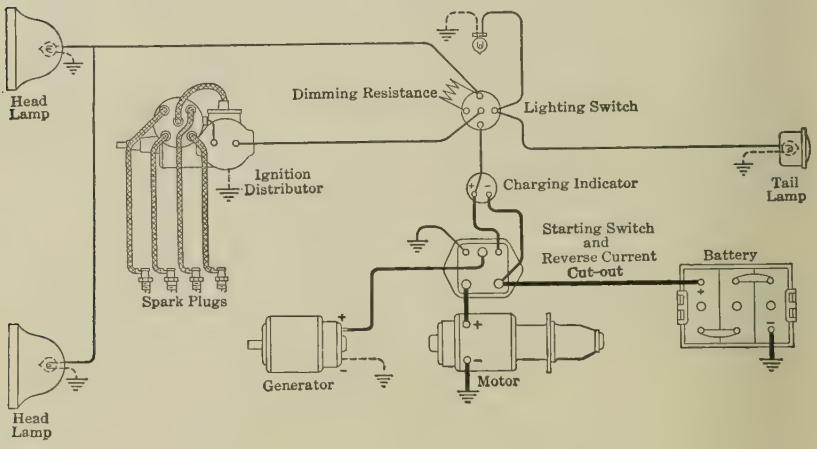


Fig. 118.—Diagram of a two-unit starting system.

of starting and lighting batteries has been brought about rapidly in recent years, with the result that a limited number of sizes, perhaps five, will accommodate more than 90 per cent of the automobiles made in this country at the present time. The special requirements of some of the old cars, however, compel battery manufacturers to make and carry in stock a considerable number of sizes for which the demand is relatively small. This increases the cost of production and often results in inconvenience to the purchaser, who must wait for special sizes which are not in the ordinary stock.

Starting and lighting batteries are ordinarily assembled with the cells side to side, as shown in Fig. 119. This is now considered the standard assembly. In some types, however, the end-to-end assembly of cells is still used. This is shown in the same figure also. Other types of the so-called irregular assemblies may consist of cells end to end in

two or more rows, or the placing of one cell across the ends of two others. The 3-cell batteries giving 6 volts are commonly used with the two-unit systems, but the 6-cell or 12-volt batteries are largely confined to the single-unit systems.

The sizes, capacities, and arrangements of the starting and lighting batteries (list of Society of Automotive Engineers) which are commonly used for service on passenger automobiles are given in the following table:

TABLE XLVII

BATTERIES FOR PASSENGER CARS AND LIGHT TRUCKS

Battery Number	Number of Cells	Minimum Capacity		Maximum Over-all Dimensions			Assembly
		5-hour Rate, Ampere-hours	20-minute Rate, Ampere-hours	Length, Inches *	Width, Inches	Height, Inches	
1	3	60	31	$9\frac{3}{8}$	$7\frac{3}{8}$	10	Side to side
2	3	72	37	$10\frac{3}{4}$	$7\frac{3}{8}$	10	Do.
3	3	84	43	$12\frac{1}{4}$	$7\frac{3}{8}$	10	Do.
4	3	96	50	$13\frac{1}{2}$	$7\frac{3}{8}$	10	Do.
5	3	95	43	$20\frac{5}{8}$	$5\frac{5}{8}$	$9\frac{1}{2}$	End to end
6	6	36	19	$12\frac{3}{4}$	$7\frac{3}{8}$	$10\frac{1}{8}$	Side to side
7	6	60	31	$17\frac{3}{8}$	$7\frac{3}{8}$	10	Do.

* Includes handles, but not the hold-down devices.

The batteries are rated at the 5-hour and 20-minute rates. This is in accord with the standardization of the Society of Automotive Engineers. However, the capacities are often given at the 5-ampere rate of discharge by the manufacturers, since this rating was in use prior to the adoption of the 5-hour rating. The 5-ampere rating does not give a satisfactory idea of the relative capacities of batteries containing large and small cells, because the 5-ampere discharge is more severe proportionately to the smaller cells than to the larger cells.

Structure.—The cells for starting and lighting batteries contain plates of the pasted variety, which are burned to the connecting straps to form the plate groups. Ordinarily there are not less than 7 plates, including 3 positives and 4 negatives, in any cell. The largest sizes of cells for 6-volt batteries may contain as many as 21 plates. The

dimensions of the plates vary greatly with the different manufacturers. The ordinary sizes are about $5\frac{5}{8}$ inches in width, 5 inches in height, and $\frac{3}{32}$ to $\frac{1}{8}$ inch in thickness. The separators for these batteries are commonly made of wood, or wood separators are combined with perforated or slotted rubber separators; but in some cases the wood separator

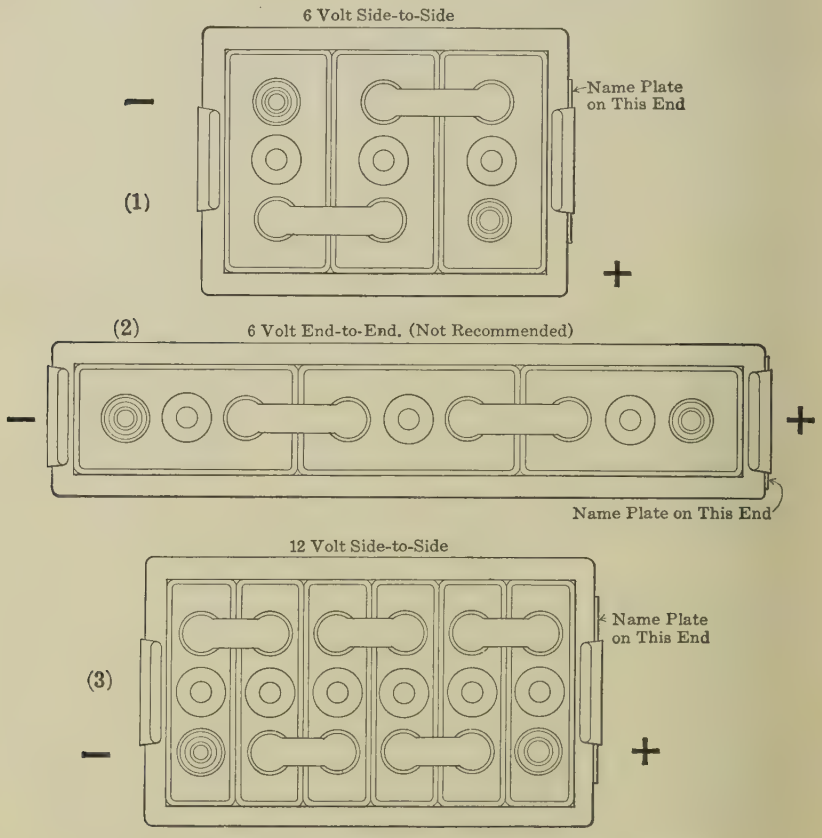


Fig. 119.—Assembly diagrams of starting and lighting batteries.

has been superseded entirely by separators made of other materials, as for example the threaded rubber separators. Separators of various kinds have been described in a preceding section (p. 36). The electrolyte consists of a solution of sulphuric acid of a specific gravity 1.280 to 1.300 when the battery is fully charged. Specific gravities higher than this are not desirable because of the local action which occurs at the negative plate and the destructive effect of the acid on

the separators. The specific gravity decreases to about 1.140 when fully discharged. A high degree of purity of the electrolyte is desirable, but perhaps not as necessary for automobile batteries as in the case of stationary or signal batteries, since the automobile batteries are charged and discharged at very frequent intervals. The temperature of the electrolyte, which also represents the temperature of the cell as a whole, should not exceed 110° F., because of the increased local action within the cell and the charring of the separators. The temperature

FIG. 120.—Starting and lighting battery.

of starting and lighting batteries will rarely rise to this figure if the charging currents are not excessive.

The jars for starting and lighting batteries are made of hard rubber compound and are either $7\frac{3}{8}$ or $7\frac{7}{8}$ inches in height and approximately 6 inches in width. The length of the jar, which is in reality the short dimension, varies with the number of plates which the cell contains. Hard-rubber battery jars for starting and lighting service on automobiles were standardized in 1918 by a joint committee of the storage battery manufacturers and the rubber industry. The plan and sections of a standard type of jar are shown in Fig. 121. The standard dimensions and designations for these jars are given in the figure and in the accompanying table:

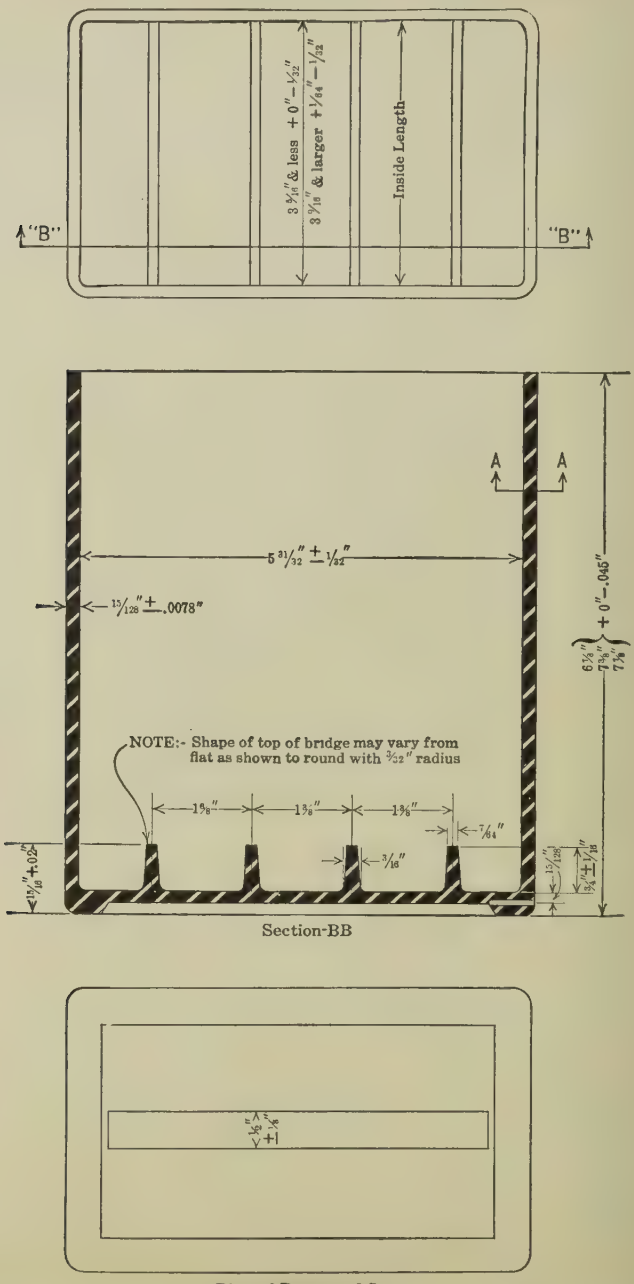


FIG. 121.—Diagram of standard jar for starting and lighting battery.

TABLE XLVIII

JAR TABULATIONS

Standard Designations		Inside Length, Inches	Standard Designations		Inside Length, Inches
Height, $7\frac{3}{8}$ Inches	Height, $7\frac{7}{8}$ Inches		Height, $7\frac{3}{8}$ Inches	Height, $7\frac{7}{8}$ Inches	
S– 1–B	S– 1–C	$\frac{15}{16}$	S–11–B	S–11–C	$2\frac{7}{8}$
S– 2–B	S– 2–C	$1\frac{1}{16}$	S–12–B	S–12–C	$3\frac{3}{16}$
S– 3–B	S– 3–C	$1\frac{5}{16}$	S–13–B	S–13–C	$3\frac{1}{4}$
S– 4–B	S– 4–C	$1\frac{1}{2}$	S–14–B	S–14–C	$3\frac{5}{16}$
S– 5–B	S– 5–C	$1\frac{11}{16}$	S–15–B	S–15–C	$3\frac{9}{16}$
S– 6–B	S– 6–C	$1\frac{15}{16}$	S–16–B	S–16–C	$3\frac{11}{16}$
S– 7–B	S– 7–C	$2\frac{1}{16}$	S–17–B	S–17–C	$3\frac{13}{16}$
S– 8–B	S– 8–C	$2\frac{3}{8}$	S–18–B	S–18–C	$3\frac{15}{16}$
S– 9–B	S– 9–C	$2\frac{7}{16}$	S–19–B	S–19–C	$4\frac{1}{8}$
S–10–B	S–10–C	$2\frac{13}{16}$	S–20–B	S–20–C	$4\frac{1}{4}$

Prior to the standardization effected by this committee, there were a total of 620 different sizes of jars in use. The action of the committee resulted in the elimination of all but 40 of these sizes.

The covers for cells of the starting and lighting type are ordinarily of molded rubber, such as is shown in Fig. 122. The cover is provided with three openings, through two of which the terminal posts of the cell project, the middle opening being used as a vent for the escape of gas when the cell is being charged. The cell may be filled with water or electrolyte by removing the vent plug. Since batteries of this type are ordinarily subjected to severe vibration, it is necessary that the vent plugs be provided with baffle plates to prevent the escape of the electrolyte, which would otherwise flood the top of the battery and gradually destroy the wooden box which contains the cells. On many of the cheaper batteries, however, vent plugs without baffle plates are used. The cells are contained in a wooden box called the tray. This is made ordinarily of a hard wood, such as oak, with the corners dove-tailed together, and further strengthened by the addition of wooden pins in the corners at top and bottom. The trays are painted, inside and out, with several coats of an acid-proof paint. The handles are commonly made of malleable metal, which is lead-coated and painted to protect

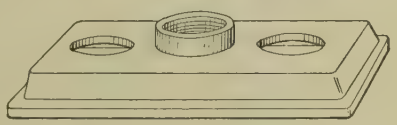


FIG. 122.—Molded cover of jar.

it from the acid of the cells. Such handles may be fastened to the box by bolts, but in some cases they are set into the wood of the tray itself and fastened by a lead casting.

The size and shape of the connectors and terminals for starting and lighting batteries are of great importance, since the batteries are required to give very large currents during the period of cranking the engine. For this reason the connectors between cells are much heavier than on the ordinary types of portable storage batteries. Solid connectors of lead or of lead-antimony alloy are used almost exclusively on batteries for service on passenger cars, but flexible copper connectors, heavily lead-coated are used on some types of batteries for truck service. The permissible voltage drop in the intercell connectors is specified by the Motor Transport Division of the Army as not to exceed 10 millivolts per inch of distance between post centers when the battery is discharging at the 20-minute rate. The resistance of the connectors will vary from 0.00005 to 0.0002 ohm per inch distance between the centers of the terminal posts of adjacent cells according to the capacity of the battery. It is obvious that if the resistance is more than a few thousandths of an ohm, the loss in voltage due to the IR drop in the connectors will be an appreciable part of the total voltage of the battery. The terminals of the battery are either straight or tapered posts. In the latter case, the size of the posts on the positive and negative cells is purposely made different to prevent wrong connections being made. The standard for such terminals is specified by the Society of Automotive Engineers as follows:

	Inch
Small diameter, negative post	$\frac{5}{8}$
Small diameter, positive post	$\frac{11}{16}$
Taper per foot	$1\frac{1}{3}$
Minimum length of taper	$\frac{11}{16}$

The polarity of the terminals should be indicated by letters or by a plus (+) sign.

The connectors which are attached to the terminals of the battery may be of either the burned-on or the clamp type. When the latter are used, some difficulty may arise owing to corrosion of the terminal, which may introduce considerable resistance into the circuit. The terminals must necessarily be kept clean.

Starting and lighting batteries at the time of sale may be filled with electrolyte and fully charged, but quite often they are in the so-called unfilled condition, by which is meant that they are not filled with electrolyte. The wood separators are moistened with water. The cells are often sealed to prevent the escape of this moisture. Some types of

batteries are shipped and sold in the so-called bone-dry condition. This is not possible with all types of separators, since many of the wood separators are subject to cracking or splitting if allowed to dry out. Separators of the threaded rubber type are not subject to deterioration in the dry condition.

d. The Service that Starting and Lighting Batteries Must Perform.

During the period of cranking an automobile engine, the battery is called upon to supply a large amount of current which, however, fluctuates rapidly in value because of the compression of gas in the cylinders of the engine. It has been possible to study the demands made upon starting and lighting batteries in the operation of various types of automobiles by using an oscillograph. Photographic records of the instantaneous values of current and voltage were obtained at the Bureau of Standards.[1] In addition to the data relative to the battery

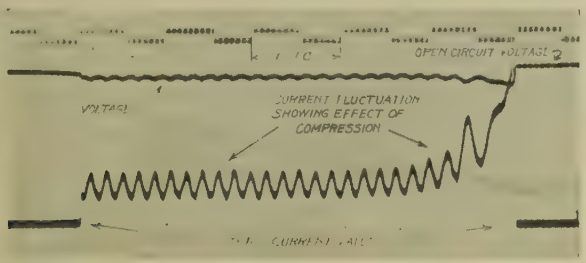


FIG. 123.—Record of the current and voltage in the battery circuit of a four-cylinder car when the starter was cranking the engine, single-unit system.

requirements, the interpretation of these records has brought out interesting facts with relation to the study of lubrication and engine problems.

The instantaneous values of current and voltage were obtained by means of a three-element moving-coil type oscillograph. In order to obtain records for periods of sufficiently long duration, the ordinary film drum of the oscillograph was replaced by a camera of special construction in which photographic paper in rolls of 100 feet could be used. When making a record the sensitized paper was wound upon a drum in the lower end of the camera after having passed the oscillograph slit, through which the recording images were projected. One of the elements was used to record the voltage at the terminals of the battery, another to record the current through the battery circuit, and the third to make the time record, which consisted of the half-second ticks of a chronometer. The general character of the curves is shown in Fig. 123. This oscillogram begins at the right and is to be read from

[1] Vinal and Snyder, Technologic Paper of the Bureau of Standards, No. 186.

right to left. The time intervals are recorded at the top of the record. The curve next below the time record represents the fluctuations of the voltage at the terminals of the battery when the starter is in operation. The last curve represents the current and shows the fluctuations due to compression in the successive cylinders. The zero value of this current is shown by the horizontal line in the lower right-hand corner. When

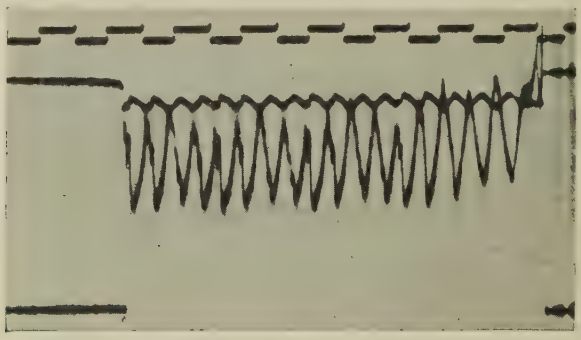


FIG. 124.—Record of the current and voltage in the battery circuit of a four-cylinder car when the starter was cranking the engine, two-unit system.

the starter pedal was pressed, the initial current during the first few hundredths of a second was approximately 125 amperes. Following this it fell rapidly. The first compression was barely visible. The second compression was followed by much lower values of current, which reached uniform values after the motor had attained a constant

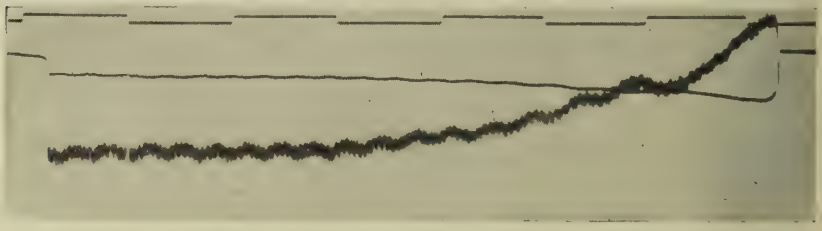


FIG. 125.—Record of the current and voltage in the battery circuit of an eight-cylinder car when the starter was cranking the engine.

speed of rotation. The curves of this figure were obtained on a four-cylinder automobile having a single-unit starting system with a 12-volt battery. In Fig. 124 is shown a somewhat similar curve for a different type of car. This car had a two-unit system operating on 6 volts. During the first half-second after closing the starting switch, the current fluctuated rapidly through a range of more than 100 amperes, the

maximum value being about 250 amperes. In this figure it can be clearly seen that the minimum values of voltage correspond to the maximum values of current. Figure 125 shows the curve obtained on an eight-cylinder car. The initial value of the current was about 425 amperes. It will be noted that the fluctuations of the current in this oscillogram are much less than in the two preceding figures. This is because of the overlapping effect of the eight cylinders.

The work which the battery has to do is determined in part by the size of the engine, which may be expressed as the number of cubic inches displacement of the pistons. The following table was given by Oetting:[2]

TABLE XLIX

Relation of Battery Size to Engine Displacement

Engine Size, Cubic Inches, Displacement	Battery Size, Ampere-hours
Up to 125	70
125 to 200	85
200 to 250	100
250 to 300	120
300 to 350	140
350 to 400	160
400 to 475	180
475 to 600	205

This table refers to the 6-volt starting batteries when the gear ratio between the starting motor and the cranking shaft of the engine is approximately in a ratio of 10 to 1. If the gear ratio is greater than 10 to 1, the size of battery can be materially reduced.

Temperature plays a very important rôle in determining the successful operation of an electric starter system. Automobiles are subjected to extremely low temperatures in winter. In some states of the United States the average temperature during the three winter months may be as low as 0° to 10° F. The low temperatures increase the viscosity of the oils, decrease the terminal voltage and capacity of the battery, and increase the difficulty in producing combustion of the gasoline vapor and air in the cylinders of the engine. The effect of the increased viscosity of the oil on the work which the battery has to do is shown in Fig. 126.[3] This figure shows the relation of the current in

[2] Journal of the Society of Automotive Engineers, 2, p. 151, 1918.

[3] Technologic Paper No. 186 of the Bureau of Standards.

the electric circuit to the viscosity of the oil used in the engine. The current which the battery delivers to the starting motor is proportional to the torque which the motor is able to exert in cranking the engine. The torque required to start any engine is obviously dependent

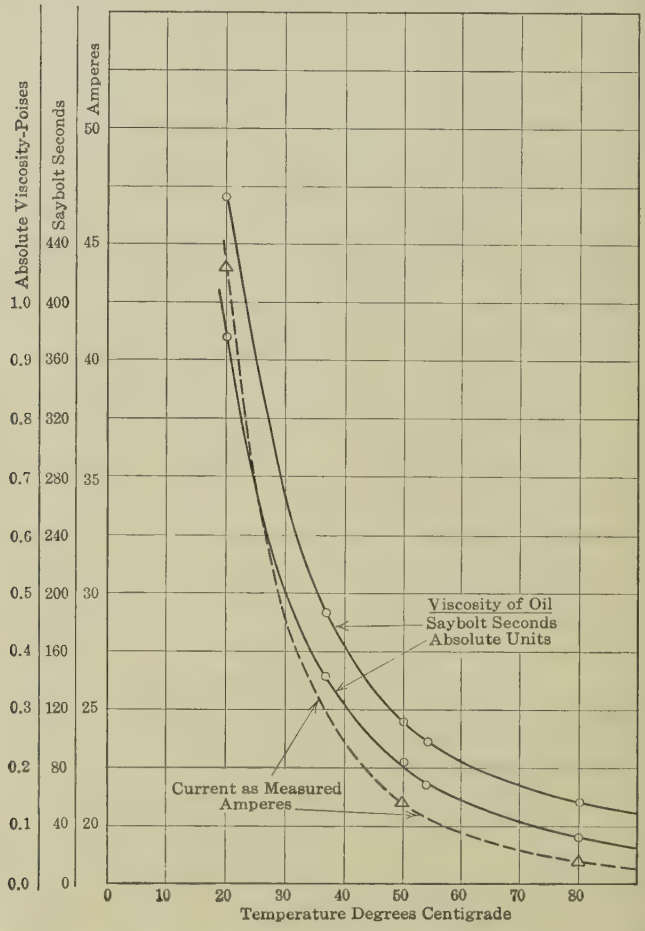


Fig. 126.—Relation of the current in the starter circuit to the viscosity of the oil in the engine.

on the friction, and therefore dependent on the viscosity of the oil which the engine contains. The data for Fig. 126 were obtained by determining the currents required to operate the engine when all compression was relieved by removing the spark plugs, measurements being made at three different temperatures. The relation of the electric

current furnished by the battery to the temperature of the engine is given by the dotted curve in the figure. The viscosity of the oil, expressed in absolute units, is given by the curve which is almost superposed upon the dotted curve.

The variation of capacity of storage batteries with the temperature has been discussed in a preceding section, p. 194. If the capacity at the temperature 80° F. is considered as 100 per cent, the capacity of the battery at 10° F. will be approximately 50 per cent. Between these limits the decrease in capacity is a linear function of the temperature. The effective or terminal voltage of the battery is also materially reduced at these low temperatures. This is not because of the temperature coefficient of the open-circuit voltage, but because of the increased resistance of the electrolyte, which causes an increased loss of energy within the cell itself. On p. 163 it was shown that the open-circuit voltage of the battery has a very small temperature coefficient. Figure 127 shows the relation of voltage at the terminals of a 6-volt starting and lighting battery to the rate of discharge when the battery is at 80° F. and at 10° F. These data have been given by Oetting.[4] The power which the battery must supply in order to break away and turn engines of various sizes at normal temperatures and at temperatures of 10° F. are shown in Fig. 128. The amount of power required varies with the piston displacement and the speed of rotation. These data have been given by Oetting.[5]

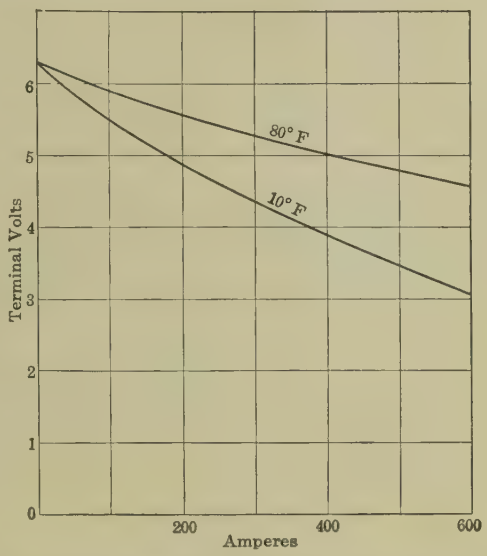


FIG. 127.—Relation of terminal volts to the current and temperature, six-volt battery.

In addition to starting the automobile engine, the storage battery is ordinarily required for lighting service. The connections of the battery to the headlights and other lights are shown in Figs. 117 and 118. The current required for lighting purposes on the ordinary auto-

[4] The Electric Journal, 16, p. 134, 1919.

[5] Journal of the Society of Automotive Engineers, 2, p. 151, 1918.

mobile varies from 4 to 10 amperes, depending upon the number of lights, but this may be materially reduced when the car is standing still if only a parking light be used. If the current required for furnishing the lights of the automobile is known, the length of time that the lights may be burned when the battery is fully charged initially may be determined approximately by dividing the ampere-hour capacity of the battery at the 5-hour rate by the current required.

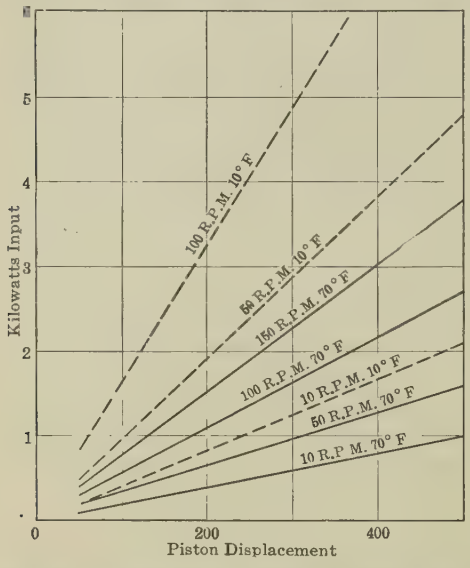


FIG. 128.—Relation of power input to the piston displacement at various speeds and temperatures.

The storage battery ordinarily furnishes the electrical energy for the ignition of the engine also. This is an intermittent service, the current being made or broken by the distributor at the required time in the cycle of each cylinder. Figure 129 shows the ignition current of a four-cylinder car which is operated slowly in order to show the details of the curve. At the left of the figure the ignition currents for the cylinders are indicated by the numbers 1, 2, 3 and 4. It will be seen that the duration of time that the current flowed through the primary coil was appreciably longer in the case of contacts

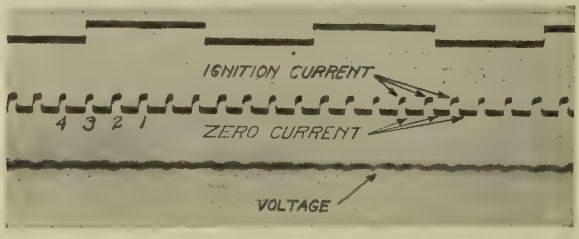


FIG. 129.—Ignition current when the engine was running slowly, four-cylinder car.

marked 1 and 2 than for those marked 3 and 4. This inequality in the action of the contact points is probably due to inequalities in the cam which operates them.

e. The Charging System.

Automobile storage batteries are charged by the action of the generator which is driven by the automobile engine. The battery is therefore charged while the car is running. The charging current which passes through the battery is not a uniform and steady current. Figure 130 shows the charging current through a 12-volt battery operated with a single-unit system. The points marked A and A' in this figure represent the operation of the reverse-current relay. Between A and B the charging current is excessive because the starter pedal had not been released until the point B was reached. The fluctuations in the charging current are due to the ignition system. These are the points which are shown in magnified form in Fig. 129. At C in the diagram the engine speed was increased. At D it was decreased and the ignition

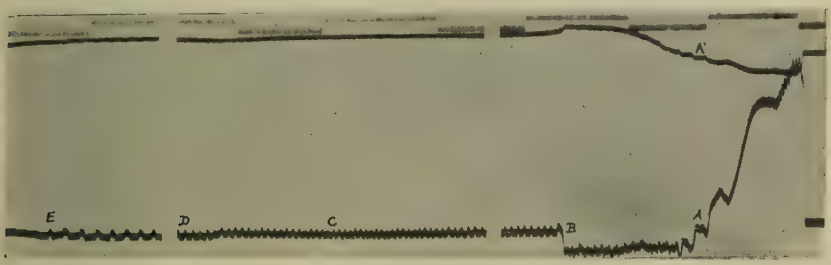


FIG. 130.—The starting of an engine with single unit system and characteristics of the charging current.

was cut off at E. The charging voltage is shown by the curve near the top of the figure. It will be noted that at the time the starter pedal was released the charging voltage was materially reduced. A similar record for a car with two-unit starting system is given in Fig. 131. Such a curve shows the instantaneous values of the charging current in a curve which is discontinuous from the current curve of the starting motor.

One of the most important factors of the charging generator is the regulation, which must be provided to prevent charging the battery at excessive currents when the automobile is in rapid motion. Ordinarily the battery will not be charged when the speed is below a certain limit. As the speed of the machine increases, the voltage of the charging generator rises, and upon reaching a definite value, which is called the cut-in voltage, corresponding to a speed of the machine of 8 to 12 miles per hour, the battery begins to charge through the operation of a suitable relay. This charging voltage ordinarily continues to rise as the speed

of the machine increases. It is necessary, therefore, to provide regulation to prevent excessive charging currents through the battery. Various devices have been used for this purpose. Among these are the slipping clutch of some of the earlier types, opposing shunt and series fields, coils of iron wire with high temperature coefficient as a ballast coil in the field circuit, limiting relays, third-brush systems, and constant-voltage regulators. The most common method in use at the present time is that which employs the third brush. This brush is ordinarily connected to the middle of the field and strengthens or weakens the field as the speed of the machine skews the magnetic field in the armature, depending upon the rate at which the armature is revolving. This system has afforded a reliable and inexpensive means of

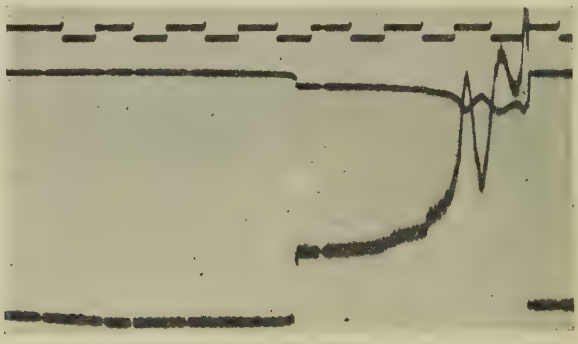


FIG. 131.—Record of starting the engine of a car with a two-unit starting system.

regulation. The characteristic charging curves of a generator having the third-brush regulation show a rapid increase in voltage with increase in speed of rotation up to a maximum point, which generally corresponds to a speed of 20 to 25 miles per hour of the automobile. If the speed of the automobile is increased beyond this point, the effect of the third brush is to reduce the field of the generator and thereby decrease the charging current, so that at high speeds it may become almost negligibly small. Such a system provides for the full charge of the battery during ordinary driving and effectively prevents the overcharge of the battery during prolonged high-speed runs when touring.

Voltage regulation of charging generators, by which is meant keeping the voltage at a constant value irrespective of the speed of rotation of the generator, has many attractive features for automobile service. This system of regulation, however, is more expensive than the third-brush system and is found only on higher-priced cars. Some of the advantages of this system, as especially applied to automobile service,

are: (1) It supplies a charging current which is dependent entirely upon the condition of the battery. If the battery is fully discharged the generator supplies a large current which charges it quickly, and the current automatically decreases to a small value when the battery becomes fully charged. (2) The constant-potential method of charging storage batteries is probably the most effective way of restoring the battery which is badly sulphated, since it prevents the building up of high potentials due to the large internal resistance of the battery, and the current is supplied only as fast as the battery is able to absorb it in the reduction of the lead sulphate on the plates.

f. Care of Starting and Lighting Batteries.

Although starting and lighting batteries are required to deliver very large currents and are often subjected to severe charging conditions, they will give satisfactory service provided they receive ordinary care and maintenance. This includes the proper adjustment of the charging system as well as the care of the battery itself.

The most convenient means of estimating the state of charge of the battery is by the hydrometer readings. A hydrometer of the syringe type will be found convenient for determining the specific gravity of the electrolyte in the cells. The measurement of the specific gravity has been described in detail on pp. 90–98. When the battery is fully charged the specific gravity will range from 1.270 to 1.300. When the battery is discharged the specific gravity will range from 1.140 to 1.160. These are the specific gravities when measurements are made at ordinary temperatures. Intermediate states of charge of a battery may be estimated by interpolating between the limits for the charged and discharged conditions.

Batteries which are used for automobile service in the tropics, require considerably lower specific gravities owing to the increase in chemical activity due to the higher temperature. It is customary to adjust the electrolyte for these batteries to a maximum value of 1.220, and this may decrease to 1.080 when the battery is completely discharged.

Hydrometer readings of each of the cells in the battery should be taken at frequent intervals. It is worth while to keep a record of the successive readings of the cells in the battery, since systematic deviations of one or more of the cells from the readings of the others usually indicates sources of trouble which should be removed. For this purpose it is convenient to number the cells, and this is customarily done by designating the cell having the positive terminal of the battery as No. 1 and the others in turn. In rare cases a false indication of the state

of charge of the battery may be given by the hydrometer readings. For example, the battery may be nearly discharged but the gravity may be fairly high. This is nearly always the result of improperly adding acid instead of water to the battery, to replace the liquid lost by evaporation. When this is found to be the case, the battery should be immediately charged and the specific gravity adjusted to the proper value.

The second essential in the ordinary care of the batteries is the addition of pure water as necessary to keep the plates well covered. The exact height specified for the electrolyte above the tops of the plates varies considerably from one manufacturer to another, but on the average $\frac{1}{2}$ inch is probably sufficient. It is desirable that the height of the electrolyte be approximately constant when taking the periodic gravity readings, as marked differences in height will result in differences in gravity not caused by the condition of charge of the plates.

The water is added to replace the so-called evaporation. By the term "evaporation" is meant not only the evaporation which takes place in the ordinary sense, but also loss of water due to gassing when the cells are on charge. It was shown on p. 82 that the relative magnitudes of the vapor pressure of the solution and the pressure of water vapor in the air determine whether evaporation in the ordinary sense will take place. Since the vapor pressure of the solution is greatly increased by a rise in temperature, more water is required to compensate for the evaporation in summer than in winter. The water should always be added after the hydrometer readings are completed. This is because the water, being less dense than the electrolyte, tends to remain on the top and give a false indication of the specific gravity. The water gradually mixes with the acid, and the electrolyte comes to a uniform density as a result of the gassing which takes place when the cells are on charge. This also suggests the necessity of making additions of water to cells in extremely cold weather before running the car, rather than after, to avoid the danger of freezing. The water is most conveniently added to the cells by the use of the syringe hydrometer. Only pure water should be added. Distilled water is much to be preferred but is not always available. As substitutes, artificial ice which has been melted in a procelain receptacle, or in some cases rain water, may be used. Rain water collected on metallic roofs is not satisfactory, and it often happens that rain water collected in the neighborhood of large cities contains considerable amounts of impurities which have been taken up by the drops of water in their passage through the air. The natural water supply can be used in some cases, but is not to be recom-

mended in general. When only natural water is available it is better to use it than to allow the battery to go dry.

Batteries for starting and lighting service on automobiles seldom require charging other than that which is received when the car is in operation. When, however, the specific gravity readings indicate that the cells are discharged and it is not possible to charge them sufficiently by running the car, it is necessary to charge them from some other source. This may be done, if direct current is available, by arranging a lamp bank as a regulating resistance. A sufficient number of incandescent lamps are arranged in parallel to allow for the necessary current, and the group is put in series with the battery and the 110-volt circuit. The charge of the battery is considered complete when, with the current flowing at the rate designated by the manufacturer, all of the cells are gassing freely and the specific gravity and the voltage have reached maximum values and maintained these values for a period of 5 hours. If the battery has been completely discharged before the beginning of the charge, it may be necessary to continue the charge for as much as 24 hours. Such a charge of the battery is desirable when the car is not in use for periods of several months at a time. Occasional charging is necessary to keep the battery in good condition. The details of battery charging are given in Chapter VI.

The fourth essential for the satisfactory operation of a starting and lighting battery is cleanliness. Water or electrolyte which has been spilled on the top of the battery should be wiped off. A rag moistened with dilute ammonia (approximately 1 to 10) or a solution of baking soda may be used to neutralize the acid on the top of the battery and the wooden tray which contains the cells. Care must be taken, however, that the ammonia is not allowed to get inside of the cells. Corrosion of the terminals, particularly the positive terminal, may be avoided by occasionally wiping the terminal with a rag moistened with ammonia water and then covering it with vaseline. Cleanliness is a factor of importance in the care of the battery since it preserves the box, prevents leakage of current from one cell to another, and insures a low resistance of the circuit, thereby affording the maximum current for starting purposes.

The temperature to which the battery is subjected is also worthy of notice. In severe cold weather the electrolyte may freeze if the specific gravity is too low, that is, if the battery is nearly discharged. The temperatures at which the solution will freeze have been given in Chapter III. It is likewise important to prevent overheating of the battery. The temperature should be kept below 40° C. (104° F.).

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Instantaneous Values of the Current and Voltage in the Battery Circuit of Automobiles, Vinal and Snyder, Tech. Paper No. 186 of the Bureau of Standards.

2. TRUCK, TRACTOR AND VEHICLE BATTERIES

a. Economic Importance.

We have reached a point in industrial development beyond which greater efficiency in the methods of handling goods must play a large part in reducing the cost to the ultimate consumer. There is abundant opportunity for increased efficiency. Obsolete methods of handling goods, whether in transport or within the factory, are industrially wasteful in as true a sense as the waste of the materials themselves. It is difficult and perhaps impossible to estimate the yearly burden of waste that results from inadequate methods of handling the raw materials, the parts, and the finished products. The estimates that have been made seem almost fantastic. Many important industrial concerns, recognizing this fact, have installed modern methods that are highly remunerative. These methods lessen the cost of manufacture, relieve congestion, and give advantage in close competition; but much still remains to be done.

Electric vehicles, whether for pleasure or for commercial purposes, have been familiar on the streets for many years. The rapid development of industrial trucks and tractors for use in factories, mines, warehouses, railroad and steamship terminals has been a more recent development. The same general type of battery is used for trucks, tractors, and vehicles, but the sizes of the individual cells which go to make up the battery vary through a rather wide range, depending on the nature of the service required. Electric vehicles have found increasing favor within recent years because of the relatively low costs for maintenance. The vehicles themselves are of simple design, having few complicated parts. This simplifies the repair work. The trucks and vehicles are free from severe vibrations and can be regulated as to speed, which minimizes accidents due to careless driving. The increased use of electric vehicles for the distribution of commodities in cities has been made possible within recent years by better surface of the streets and improved batteries.

b. Classification of Trucks, Tractors and Vehicles.

Industrial trucks were originally designed for use in railway stations for the transportation of baggage. These trucks combined in a single unit the battery for motive power and the loading space. The next step in providing for heavier traffic was to divide the functions of these platform trucks. The load to be transmitted was placed upon trailers which were drawn by an electric tractor.

Figure 132 shows an electric industrial tractor designed for hauling heavy trains of trailers. These tractors are short, sturdy, and com-

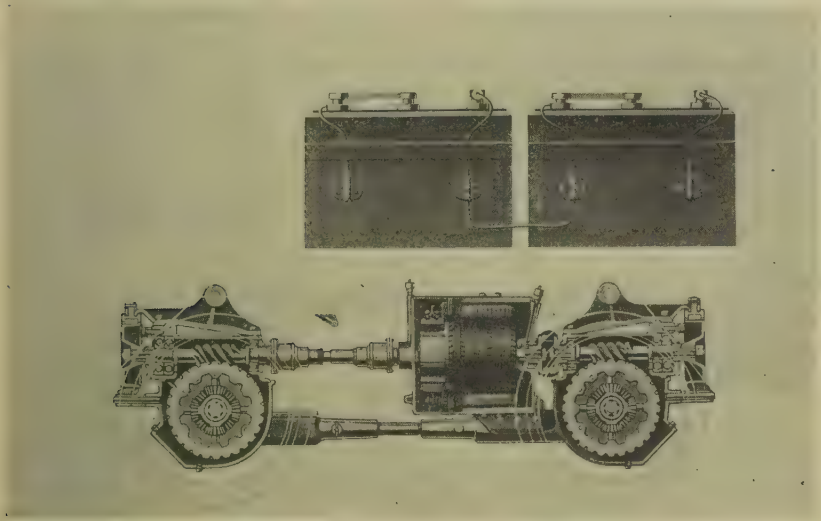

FIG. 132.—Electric industrial tractor, showing the battery and the driving mechanism.

pact units with rubber-tired wheels carrying only the battery and the driver. The length is usually about 7 feet, the width 4 feet, and the height $4\frac{1}{2}$ feet. They weigh approximately 1 ton, to which the batteries will add 1000 to 1500 pounds, depending on the size and type. The tractors are ordinarily made with a short wheelbase of about 42 inches. The turning radius of the tractors is about 10 feet on the outside edge, or may in some cases be less. The battery is contained in the compartment over the driving wheels and usually consists of 24 cells of the lead-acid type or 42 cells of the nickel-iron (Edison) type. When the tractor is unloaded it may attain a speed of about 7 miles per hour, but when drawing a load the speed is reduced to 4 or 5 miles per hour.

The train of trailers usually numbers three or more. Figure 133

shows a tractor and trailers. These trailers normally carry about 4000 pounds each. One of the essential features in designing trailers for this service is to make them follow accurately the path traversed

FIG. 133.—Tractor pulling a train of trailers.

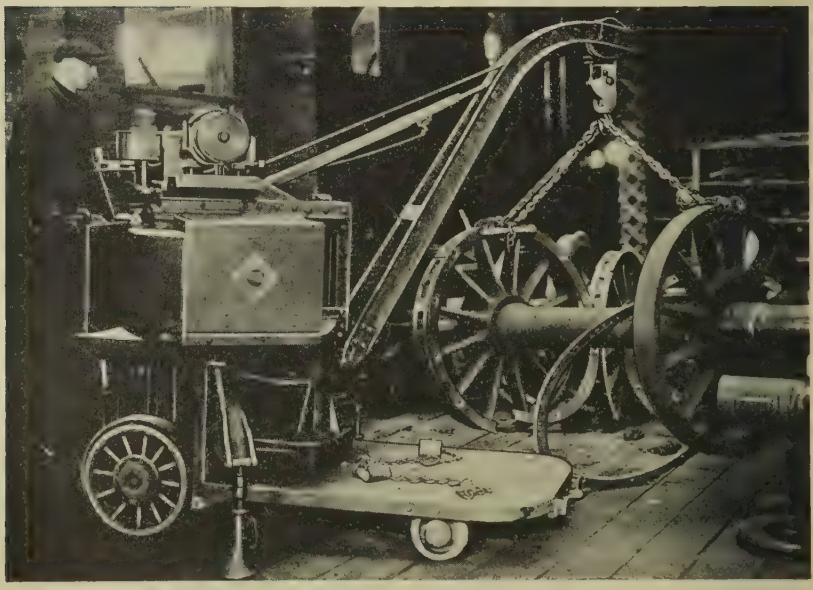

FIG. 134.—Electric platform truck with crane.

by the tractor itself, since these trains are often required to operate in factories or terminals where the passageways are narrow and turns frequent. Figure 134 shows an industrial truck equipped with a

crane for picking up the load and depositing it upon the platform of the truck. This crane is operated by a motor which is separate from the running gear of the tractor, but one battery serves for operating both the truck and the crane. The battery for this type of truck is carried in the box behind the driver's stand. Another modification of such a truck is found in the elevating-platform type. The platform of these trucks may be raised a few inches, permitting them to pick up loaded platforms of material with a minimum expenditure of time. A number of specialized trucks and tractors have been devised to meet

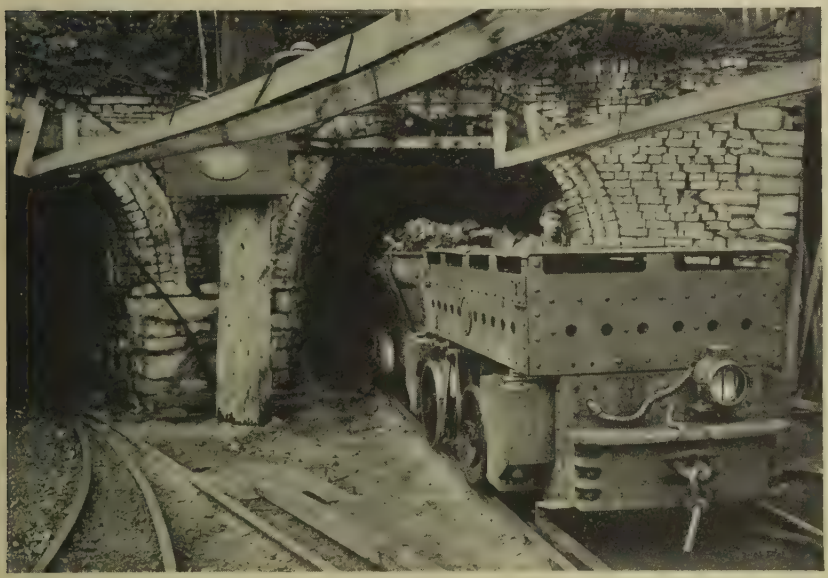

FIG. 135.—Electric mine locomotive. The battery is in the compartment in front of the driver.

the different needs of various kinds of manufacturing. Those which have been described, however, are typical of the general class.

An important form of electric locomotive is that used in mines and commonly called the mine locomotive. A locomotive is distinguished from a tractor by the fact that it runs on rails, while a tractor has rubber tires, stearing mechanism, differential, etc. The locomotives are compact units of minimum height which carry the battery for motive power and are capable of pulling a train of loaded trailers. Mine locomotives are rapidly replacing the animals which were previously used for transporting material within the mines. A picture of a mine locomotive is shown in Fig. 135.

c. The Batteries.

The batteries used for propelling trucks, tractors, and vehicles are of either the lead-acid or the nickel-iron type. Typical batteries of these kinds, for use in trucks, are shown in Figs. 137 and 138. The lead-acid batteries contain plates which are usually $5\frac{3}{4}$ inches in width (14.6 cm.) by $8\frac{5}{8}$ inches (21.9 cm.) in height. The positive plates vary from .43 inch (1.09 cm.) to .13 inch (.33 cm.) in thickness. The negative plates vary from .20 inch (.51 cm.) to .11 inch (.3 cm.). The negative plates are naturally made thinner than the positives.

For certain types of vehicle service, thin-plate batteries have been extensively used. This is particularly true of pleasure vehicles, for

Fig. 136.—Electric truck for hauling lumber.

which the conditions of service are not as severe as for the trucks and tractors. The thin plates in these cells do not have a greater capacity per plate than the thick plates of the same length and width. The capacity of the thin plates is actually less, but because a larger number of these plates can be used within a jar of given size, the capacity of the cell at the higher rates of discharge is considerably greater (see p. 185).

Rubber jars for the cells have been standardized by the Society of Automotive Engineers. These jars have a width of $6\frac{1}{8}$ inches and an over-all height of $13\frac{5}{8}$ inches. The extra height makes possible the use of the so-called high ribs in the bottom of the jar, which support the plates and provide space for the accumulation of sediment as it

sifts down from the plates. These ribs are $2\frac{3}{4}$ inches in height. Some of the jars are provided with two ribs, and others with four. In the

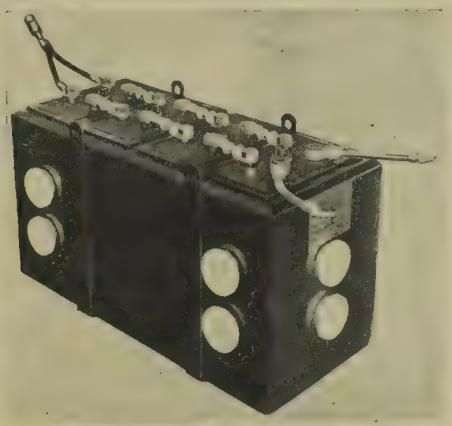

FIG. 137.—Locomotive battery of the lead-acid type. This battery has four cells of thirty-three plates with double posts and connectors. The connectors are burned to the positive posts and bolted to the negative posts.

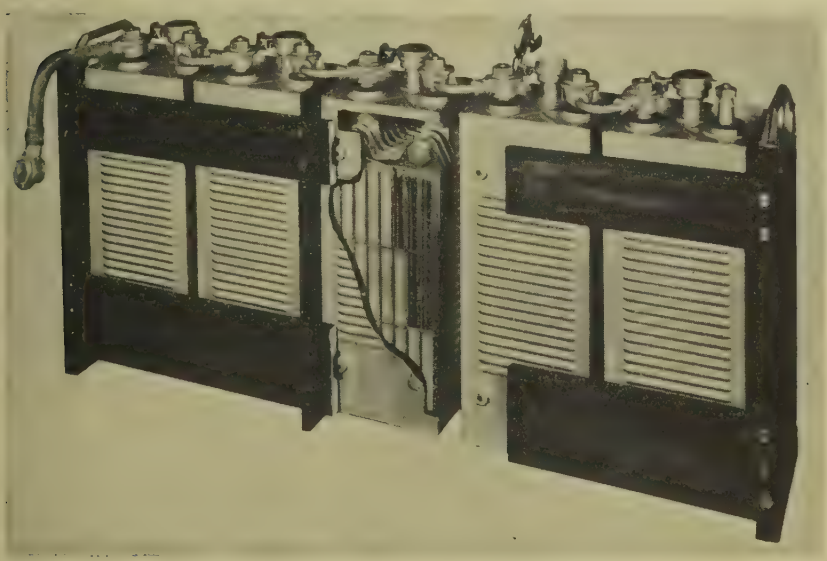

FIG. 138.—Edison battery for trucks, tractors and vehicles; type A8.

latter case it is customary for the positive plates to rest on every other rib and the negative plates on those which come between. There are

fifteen sizes of the rubber jars, of lengths varying from $2\frac{5}{16}$ inches to $5\frac{3}{4}$ inches.

Connections between individual cells of a tray are known as intercell connectors, and similarly the connections between the trays are known as intertray connectors. These may be either burned or bolted to the cells. Burned-on connectors are generally preferred, since the acid may creep in between the contact surfaces of the bolted connection and cause corrosion, which will destroy the joint electrically.

The intercell connectors may be either copper straps heavily lead-plated or solid connectors of the lead-antimony alloy. The copper straps, which are sometimes subject to corrosion, have the advantage of flexibility and high conductivity. A loop in the middle of these straps allows for expansion and for a slight movement of the cells without danger of cracking the covers. The design of the intercell connectors is a matter of considerable importance, since the drop in voltage when the battery is required to give large current drains may become an appreciable part of the total available voltage of the battery. The power which is lost in the intercell connectors increases with the square of the current which the battery delivers. This power loss for low rates of discharge is entirely negligible, but at high current rates, such as may be required when a tractor is pulling a heavy load up a steep ramp, may amount to $\frac{1}{2}$ hp. or even more. Table L shows the power loss for intercell connectors on a battery of excellent design. This table shows a hundredfold increase in the power loss as the discharge current is increased from the normal value of 45 amperes to 10 times the normal rate, or 450 amperes.

TABLE L

Power Loss in Intercell Connectors

Type and Number of Cells	Discharge Current	Drop in Voltage	I^2R Loss, Watts
Lead-acid Batteries, 12 cells (11 connectors)	45	0.053	2.37
	90	0.106	9.5
	225	0.264	59.0
	450	0.528	237.0

In the case of starting and lighting batteries, a limit has been specified for the drop in voltage in the intercell connectors in the specifications adopted by the Motor Transport Division of the Army. The specification and the method of making the test are described on page

323. It would be possible to prepare a similar specification for the truck, tractor, and vehicle batteries to insure satisfactory service.

The batteries that have found the widest use for truck and tractor service are the Exide-ironclad, the flat-plate " Philco " batteries, and

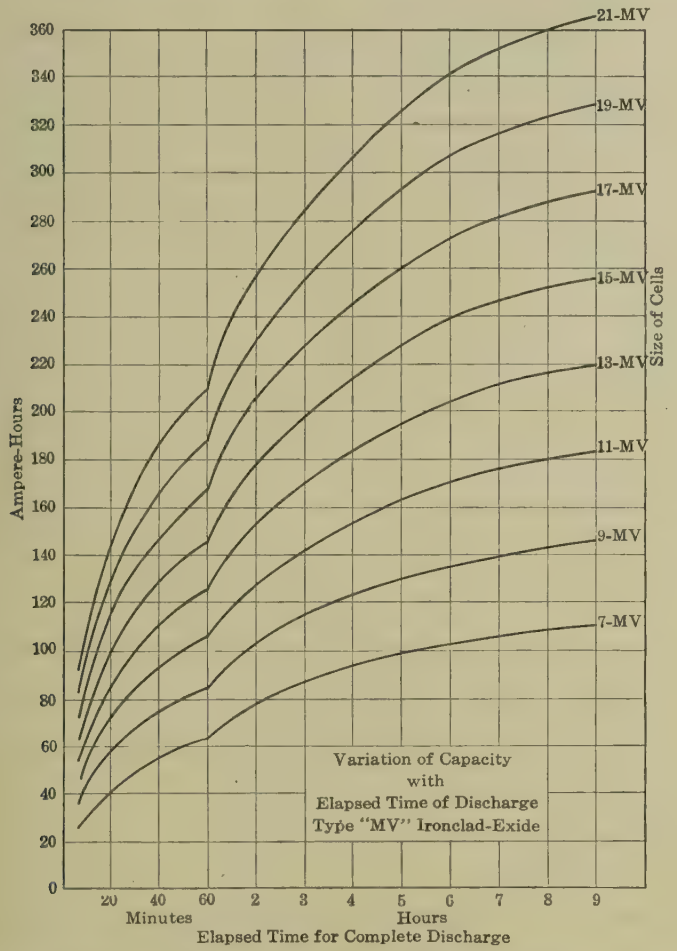

Fig. 139.—Variation of capacity with the rate of the discharge and the size of the cell.

the Edison batteries. Table LI gives the weight, dimensions, capacity, and other necessary information for the operation of cells of the Exide-ironclad type. This table is based upon information published by the manufacturer. The capacity and power output at other rates of discharge may be obtained from Figs. 139 and 140.

In Table LII are given data for the Edison storage batteries, also based upon information furnished by the manufacturer. The Edison cells used for truck, tractor, and vehicle service are described as types

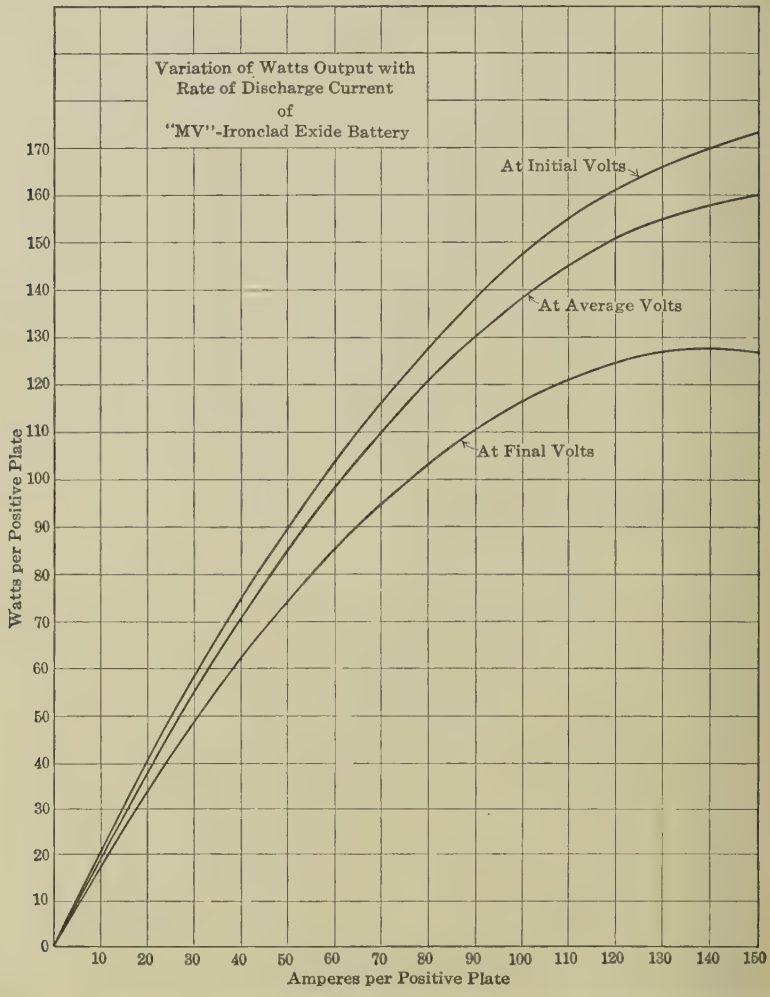

FIG. 140.—Variation of power output with the rate of the discharge and the terminal voltage.

A and *G*. The difference between these lies in the number and size of the tubes which are in the positive plates. For the *A*-type cells, there are thirty tubes $\frac{1}{4}$ inch in diameter in each positive plate. The *G*-type plates, on the other hand, have forty tubes each $\frac{3}{16}$ inch in diameter.

TABLE LI

Data on Exide Ironclad Batteries for Truck, Tractor and Vehicle Service

The data are given on the per cell basis. The ampere-hour efficiency at 5-hour rate is 88 per cent; the watt-hour efficency 74 per cent.

	MV 7	MV 9	MV 11	MV 13	MV 15	MV 17	MV 19	MV 21	MV 23	MV 25*
Number of positve pates	3	4	5	6	7	8	9	10	11	12
Weight of cell, pounds	23.75	30.0	36.5	42.75	49.5	57.25	63.5	70.0	76.25	82.75
Weight of battery, per cell	27	34	41	48	55	64	71	78	85	93
Length of cell, inches	2.87	3.56	4.31	5.06	5.87	6.62	7.37	8.12	8.87	9.62
Width of cell, inches	6.19	6.19	6.19	6.19	6.25	6.25	6.25	6.25	6.25	6.25
Height of cell, inches	15	15	15	15	15.06	15.06	15.06	15.06	15.06	15.06
Capacity, 5-hour rate:										
Ampere hours	98	130	162	195	227	260	292	325	357	390
Watt-hours	194	258	321	386	450	515	579	644	717	772
Average voltage:										
5-hour rate	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98	1.98
Weight of electrolyte, pounds	4.25	5.5	6.75	8.00	9.25	10.5	11. 75	13.0	14.25	15.5
Charging rate:										
Start amperes	19	24	30	35	40	45	51	56	61	66
Finish amperes	8	10	12	14	16	18	20	22	24	26

* These batteries are also made with 27, 29, 31, 33, 39 and 41 plates.

TABLE LII

Data on Edison Storage Batteries for Truck, Tractor and Vehicle Service

The data are given on the per cell basis. The normal charging rate is the same as the 5-hour discharge rate. Ampere-hour efficiency 82 per cent; watt-hour efficiency 60 per cent at 5-hour rate.

	A 4	A 5	A 6	A 8	A 10	A 12	G 4	G 6	G 7	G 9	G 11	G 14	G 18
Number of positive plates	4	5	6	8	10	12	4	6	7	9	11	14	18
Weight of cell, pounds	13.8	16.7	19.4	26.8	33.3	40.6	10.9	15.1	17.4	21.1	27.3	34	44.5
Weight of battery, per cell	14.9	17.5	20.8	29.0	36.2	43.9	13.0	16.8	18.2	23.0	29.6	36.9	47.8
Length of cell, inches	2.64	3.19	3.80	5.03	6.15	7.39	2.05	2.89	3.32	4.08	5.03	6.15	8.01
Width of cell, inches	5.13	5.13	5.13	5.20	5.45	5.45	5.11	5.13	5.13	5.13	5.20	5.45	5.45
Height of cell, over-all	13.38	13.38	13.38	14.00	14.00	14.59	13.38	13.38	13.38	13.38	14.00	14.00	14.59
Capacity, 5-hour rate:													
Ampere-hour	150	187.5	225	300	375	450	100	150	175	225	275	350	450
Watt-hour	180	225	270	360	450	540	120	180	210	270	330	420	540
Discharge rates (amperes):													
8 hours to 1 volt	18.75	23.44	28.13	37.5	46.88	56.25	12.5	18.75	21.87	28.12	34.37	43.75	56.15
5-hours to 1 volt*	30.00	37.5	45.0	60.0	75.0	90.0	20	30	35	45	55	70	90
1 hour to 0.6 volt	140	175	210	280	350	420	93	140	163	210	257	327	420
Average voltage:													
8-hour rate (volts)	1.24	1.24	1.24	1.24	1.24	1.24	1.25	1.25	1.25	1.25	1.25	1.25	1.25
5-hour rate (volts)	1.20	1.20	1.20	1.20	1.20	1.20	1.23	1.23	1.23	1.23	1.23	1.23	1.23
1-hour rate (volts)	0.87	0.87	0.87	0.87	0.87	0.87	1.01	1.01	1.01	1.01	1.01	1.01	1.01
Effective resistance, ohms	0.003	0.0024	0.002	0.0015	0.0012	0.001	0.003	0.002	0.0017	0.0013	0.0011	0.0009	0.0007
Electrolyte, pounds	3.1	3.6	4.1	6.1	7.7	9.4	2.35	2.87	3.55	4.22	5.81	7.16	10.15

* Normal charging rate same as 5-hour discharge rate.

The G-type batteries are of somewhat lower internal resistance than the A-type and are intended for service where the current drain on the battery may at times be very heavy. The connections between the cells consist of heavy copper wire swaged into steel lugs having an inside taper which fits the taper of the terminal posts of the cells. More of these connectors are necessarily used for the Edison battery than for the lead type, since 21 Edison cells correspond approximately in voltage to 12 cells of the lead type. In spite of this fact, however, the average drop in voltage within the connectors exceeds that for the lead cells by only a slight amount. The Edison cells are assembled in hard wood crates which are provided with recessed hard rubber buttons into which fit the bosses on the individual cells. They are therefore held rigidly in position with a slight space between each cell to provide the necessary insulation.

The life of the batteries in service is of great importance in determining the cost of operation. For electric trucks, such as are used in express service, the average life of the Ironclad battery is about thirty-four months. The Edison battery gives approximately twice this length of service. The actual period of service which may be obtained in any kind of work will vary with the care the battery receives.

d. The Service which the Battery has to Perform.

The electric vehicle differs from the gasoline truck in the matter of starting torque. The torque of the motor on the electric truck increases as the speed of the truck decreases, that is to say, the torque is a maximum when the truck is beginning to move. The gasoline engine, on the other hand, delivers its maximum torque at high speeds. The performance of an electric truck as compared with a gasoline truck at *low speed* is therefore in favor of the former.

The tractive effort of the truck is the force required to overcome the resistance of the vehicle and its load to motion. Drawbar-pull is a term applying to the trailing load, and is usually expressed as pounds per ton of the total weight of the load. The drawbar-pull varies with the surface over which the vehicle moves, the grades which it encounters, and the speed of the vehicle. Figure 141 shows the relation of the drawbar-pull to the amperes which the battery discharges. From this it is evident that the drawbar-pull increases as the current increases. The voltage of the battery, on the other hand, decreases and consequently the speed of the vehicle decreases. In Fig. 141 the relation of the current to the voltage and to the speed is shown for a tractor equipped with one type of battery. The speed may exceed 8 miles per

hour, but under the heaviest load conditions this may fall to less than 1 mile per hour.

The variation of the drawbar-pull with the surface over which the vehicle passes is shown in Table LIII, which has been taken from an article by Pace.[6]

Pace states that the drawbar-pull is increased 20 pounds per ton of load for each 1 per cent of up-grade. When the vehicle is going on a down-grade, however, an allowance of 20 pounds per ton may be made

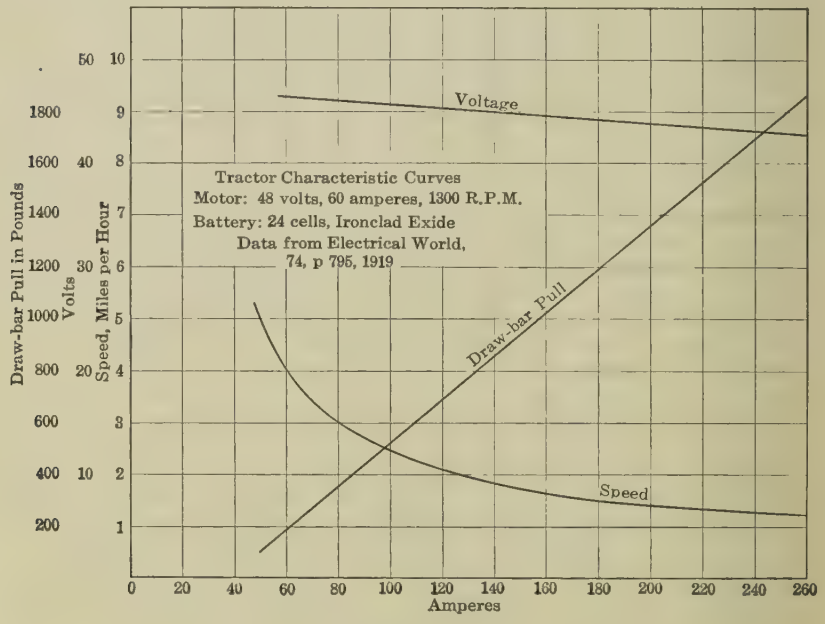
Tractor Characteristic Curves
Motor: 48 volts, 60 amperes, 1300 R.P.M.
Battery: 24 cells, Ironclad Exide
Data from Electrical World,
74, p 795, 1919
Voltage
Draw-bar Pull
Speed
Draw-bar Pull in Pounds
Volts
Speed, Miles per Hour
Amperes
0 20 40 60 80 100 120 140 160 180 200 220 240 260
200 400 600 800 1000 1200 1400 1600 1800
10 20 30 40 50
1 2 3 4 5 6 7 8 9 10

FIG. 141.—Operating curves of a tractor.

for each per cent of down-grade. From the data which are given it is possible to compute the drawbar-pull required for any given load conditions.

The service which a vehicle or tractor performs is measured in terms of ton-miles per hour, the ton-mile being a unit which corresponds to the transportation of one ton through a distance of one mile. The quantity "ton-miles per hour" is therefore a measure of the transportation service which the truck or tractor can render. This varies with the amount of the load and the grade along which it passes. It depends also on the size, the design, and the construction of the vehicle.

[6] Electrical World, 74, p. 795, 1919.

The maximum number of ton-miles per hour is not, however, a sufficient guide in choosing a truck, tractor, or vehicle, unless it is considered in connection with the requirements of the work to be performed. For example, a given tractor may have a large transportation capacity because it can haul a very heavy load at a low speed, but this would not be suitable for use where small or medium loads must be transported rapidly. Or again, two tractors may be capable of drawing equal loads, but one of these may exceed the other in ton-miles per hour because of greater speed. In some cases the high speed may be objectionable, as where frequent curves occur or obstacles are to be avoided. If the high-speed tractor cannot be operated efficiently at low speed in such places, the tractor of lower transportation capacity may prove to be better adapted to the service. The question of the ton-miles per charge of the battery is also an important item to consider.

TABLE LIII

Road Resistances Encountered with Trailers

Type of Road Surface: Resistance (Pounds per Ton)		Type of Road Surface: Resistance (Pounds per Ton)	
Asphalt, hard	28	Snow, soft	66
Brick, smooth or cement floor	40	Gravel road	75
Brick, poor	57	Poor, macadam	75
Brick, glazed	47	Clay	200
Macadam	47	Sand road	275
Tarvia	47	Loose sand, 3 inches deep	330
Granite blocks	56	Concrete road	36
Wood blocks	40	Poor concrete	53
Snow, hard	50	Wood planking	43
Ice and snow	40	Wood, planking, sticky surface	57

The quantity " watt-hours per ton-mile " represents the consumption of energy from the battery per unit of material transported. This is an important factor in determining the cost of the electrical energy required for accomplishing the given transportation result. It is the amount of energy taken from the battery per unit of transportation service, that is, for one ton carried one mile. For any tractor or truck, it obviously increases as the grade increases; and for any specified grade, it will be smaller in proportion as the efficiency of the vehicle is increased. The cost of electrical energy per ton-mile cannot be found directly from the watt-hours per ton-mile that are consumed and the price paid per kilowatt-hour, because the energy efficiency of the battery and the

charging apparatus must be taken into account also. Figure 142 shows the relation of the watt-hours per ton-mile and the ton-miles per watt-hour to the load which the tractor hauls on a level surface. These curves represent the result of test of a particular type of tractor, but the performance of different types will vary considerably. Using Fig. 142, a rough estimate of the size of battery required for a given service may be made. For example, if the total load is 20,000 pounds, Curve 2 shows that on a level surface the tractor can move 47.5 ton-miles per hour and that the corresponding energy consumption per ton-mile is

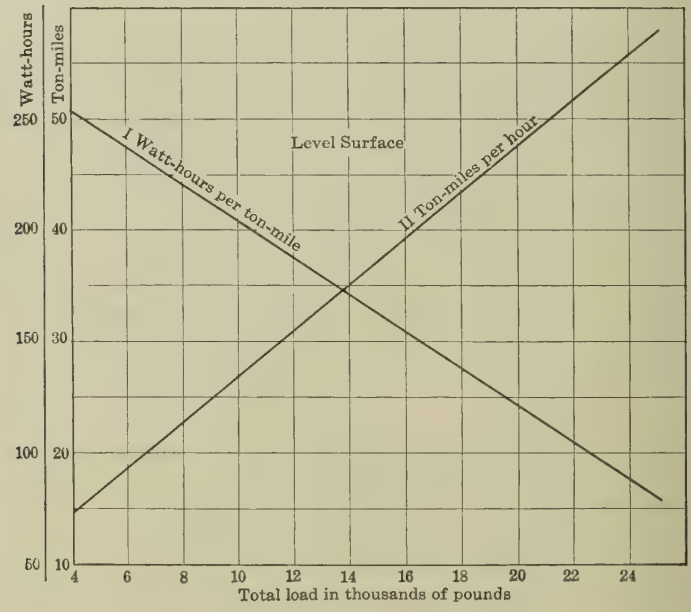

Fig. 142.—Energy consumption and transportation ability of a tractor.

120 watt-hours. The energy consumed per hour is therefore 5.7 kilowatt-hours. This figure may now be applied to the data which have been given in Figs. 139 and 140, to estimate the length of time that the battery can operate the tractor; but it must be remembered that the service which is ordinarily performed is intermittent and therefore the period of service will be longer than the figures indicate, depending on the nature of the service and the current which the battery is required to discharge. A comparison of the capacities of three types of batteries on continuous service and intermittent service is given in the following table.

TABLE LIV

COMPARISON OF KILOWATT-HOUR CAPACITIES OF TRACTOR BATTERIES FOR CONTINUOUS AND INTERMITTENT DISCHARGE

Type of Battery	At 45 Amperes				At 225 Amperes		
Kind of Plate	No. of Positive Plates	Continuous Discharge	5 Minutes on; 5 Minutes off	Per Cent Increase	Continuous Discharge	2 Minutes on; 10 Minutes off	Per Cent Increase
Lead, ironclad*.	7	5.90	6.62	12	2.98	4.18	40
Lead, flat plate*	8	5.66	6.44	14	2.85	3.64	28
Nickel-iron†...	6	5.32	6.46	21	3.02	3.78	25

* 12-cell battery.
† 21-cell battery

In Fig. 143 are shown curves of the velocity and acceleration of a tractor drawing a 5-ton load up a 2.8 per cent grade. These curves were made by first determining the time-distance curve as the tractor traveled along a row of pegs located at certain intervals. The time that each peg fell was automatically recorded on a chart, which permitted an estimate of the time, to within .01 of a second, to be made. The time-distance curve was then differentiated, giving the velocity curve, and this in turn was differentiated to give the acceleration curve. In the figure it will be seen that the velocity increases very rapidly during the first 3 seconds and after this more slowly, reaching a maximum value at the end of 12 seconds. The acceleration curve shows a sharp break at the end of 1 second. The exact cause for this is not known, but it is supposed to have been due to taking up the slack in the connection between tractor and trucks. The curve of acceleration decreases rapidly as the velocity of the truck increases, and it eventually comes to a zero value at the time that the velocity has reached its maximum steady value. A series of curves, such as is shown in the figure, for different types of tractors equipped with different types of batteries, permits an accurate comparison to be made between them.

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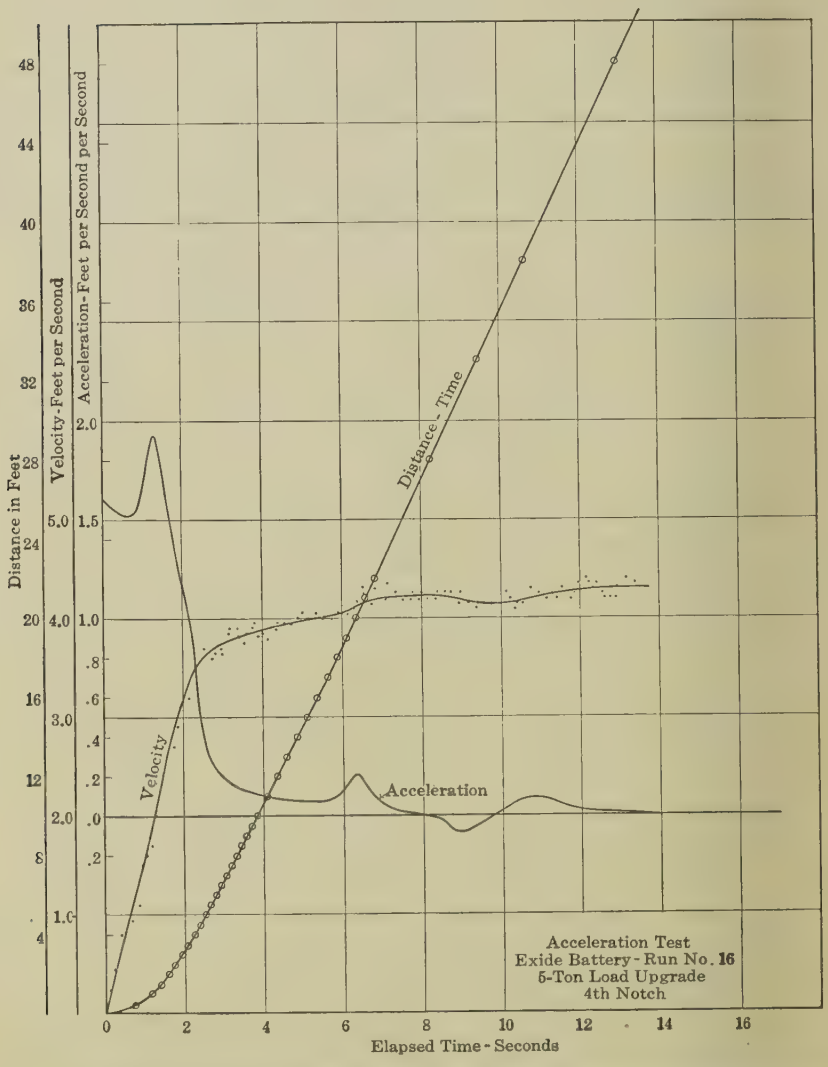

FIG. 143.—Velocity and acceleration curves of an electric tractor drawing a five-ton load.

3. TRAIN-LIGHTING BATTERIES

The earliest attempts at lighting railway cars by electricity were made in 1881, but the active development of car-lighting systems may be said to have begun in 1900. Electric car-lighting is confined to passenger trains and trains made up of express, mail, or baggage cars; electric lighting of freight trains is confined to the locomotive.

One of the most important factors which has contributed to the rapid development of railway train lighting has been the introduction of the new metal-filament electric lamp. At the beginning, the lamps used were rated for 60 to 64 volts, but with the introduction of axle-driven generators and tungsten lamps, this value has been reduced to 30 to 32 volts. This reduction has been made possible because of the decreased line drop and the increased efficiency of the lamps. The lamps now used in train-lighting service vary from the 10- to the 50-watt size. The most common sizes, however, are 25 and 15 watts. These lamps differ in voltage from those used on cars of electric roads, where lamps of 110 volts or higher are employed. The voltage of the train-lighting systems, with few exceptions, has always been less than 110 volts because it has been economical to keep the number of cells in the battery as low as possible. In some foreign countries, voltages as low as 24 volts are found.

The illumination requirements for the different types of cars vary according to the service. No standardization has been effected, except in the case of Pullman cars, but the requirements dictated by good engineering practice are believed to fall within the following limits: for baggage cars, an illumination of 4 to 6 foot-candles; for mail cars, in the central part, 5 to 10 foot-candles; for day coaches, 4 to 8 foot-candles; for parlor cars, 4 to 8 foot-candles; for sleeping cars, 4 to 8 foot-candles, with the addition of berth lights consisting of 15-watt lamps and night lights to illuminate the aisles, usually of 10-watt lamps. For dining cars, 4 to 6 foot-candles are required for the general lighting, and this is supplemented by local table lighting. The illumination requirement is an important factor in determining the size of the battery which is required.

a. Description of the Batteries.

Batteries of the lead-acid type used for train lighting (Fig. 144) may be either of the Planté or pasted varieties. Sometimes a combination of Planté positive plates with pasted negatives is used also, for the reason that the Planté positives are considered to have a longer life under the

severe conditions of service than the pasted positives. The sizes of the batteries may range from 120 ampere-hour capacity, as used on some baggage cars, to 540 ampere-hour capacity, occasionally found on mail cars. The size most commonly used is the 300 ampere-hour battery. The batteries consist of 15 or 16 cells for the 32-volt systems or 32 cells for the 64-volt systems. The latter are now being rapidly replaced by the lower voltages.

The containers for the car-lighting batteries may be rubber jars, or may consist of two-compartment wood tanks with lead linings or two cells in lead tanks mounted in a crate. The linings are made of heavy sheet lead and surmounted by a crown which reinforces the top and provides a support for the cover and space for the sealing compound. The wood compartments or crates are usually provided with porcelain rollers or skids to facilitate moving the batteries, and porcelain cleats to serve as spacers and insulators are frequently placed on the sides.

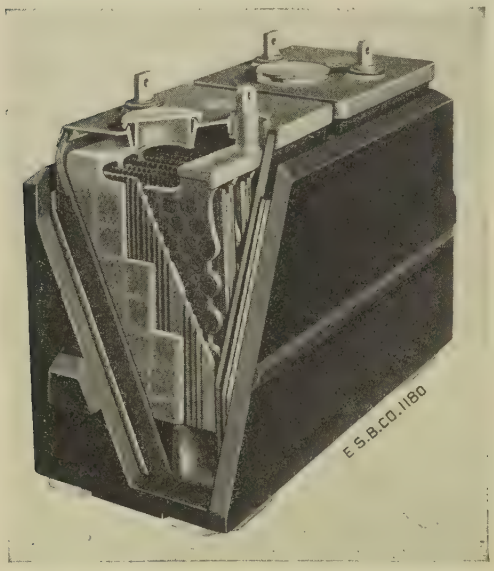

FIG. 144.—Two-cell unit of a car lighting battery of the lead-acid type.

The plate groups of the 300 ampere-hour lead batteries comprise 6 positive plates and 7 negatives. The size of plate varies somewhat from one manufacturer to another, but is about $7\frac{3}{4}$ inches by 10 inches on the average. The separators are generally of wood, heavily corrugated, in some cases being corrugated on both sides. Perforated rubber separators with reinforcing ribs are also used by some manufacturers. The plates are supported on porcelain plate rests at the bottom of the cells. These serve to carry the weight of the element and at the same time provide insulation from the lead lining and a sediment space. The covers of the cells are made of hard rubber or of the alloy of lead and antimony. The covers provide space for sealing, openings for the posts from the connecting straps, and a large vent with gas outlet.

The electrolyte used for car-lighting batteries consists of a pure solution of sulphuric acid of specific gravity of about 1.220, the limits for any one type of battery being determined in accordance with the practice of the manufacturer. The intercell connectors are of rubber-covered wire of a size ranging from No. 6 to No. 2.

Edison batteries for train-lighting service are of standard car-lighting type, *A8H*, of 300 ampere-hour capacity, but other sizes used range from the *A4H* to the *A12H*. The normal set of Edison batteries for 32-volt systems consists of 25 cells and contains 3 cells to a tray for 8 trays and one additional tray containing a single cell. The Edison type-*A8H* cells differ from the more usual type *A8* merely in the extra height of the can. An additional space of 3 inches is provided for electrolyte. This is a desirable feature for batteries in train-lighting service because flushing is required less often.

b. Location of the Batteries.

Batteries are installed in boxes, beneath the body of the car near the center. The front face of the box, which serves also as a door, is about 6 inches back from the outside edge of the car. The supports for the battery boxes pass underneath the bottom of the box, in order to carry the heavy weight of the battery. The wood is saturated with some material, as with equal parts of paraffin and beeswax or rosin, to make it impervious to the electrolyte of the battery. Boxes are ventilated to prevent accumulation of the gases during charge. The hinged covers of the boxes, when lowered, serve as a shelf upon which the cells may be drawn forward for inspection and minor repairs.

c. Principal Systems of Car Lighting.

The Straight Storage System.—The earliest system developed was the straight storage system which consisted of a battery on each car to provide current for the lights on that car irrespective of the other cars in the train. The voltage of the straight storage system was 32 or 64 volts, the latter being the more common. Charging of batteries on these cars was done at the terminals or division points of the line during the lay-over period. Polarized charging plugs were provided on either side of the car. The chief advantage of this system is simplicity. One disadvantage is the extensive charging equipment required at the terminals, which must necessarily have a large current capacity if the batteries on many cars are to be charged at the same time; but a more serious disadvantage, from the operating standpoint, is the necessity for spotting the cars on which batteries must be charged

and permitting them to lay over for a sufficient time to fully charge the battery. The cars are productive of revenue only when in actual service, and the charging period therefore decreases the possible earning power. The straight storage system is said to be the most expensive system to operate in spite of its extreme simplicity.

Head-end Systems.—The head-end systems consist of a generator on the baggage car or locomotive, driven by a reciprocating engine or turbine supplied with steam, at reduced pressure from the locomotive. The earliest forms of this system did not include a battery. Failures in the lighting were frequent and were necessarily caused every time the train was parted or the locomotive uncoupled. For this reason, in the later developments of this system the addition of the batteries was found necessary. Sometimes only two or three batteries were provided for the entire train, but generally a battery was provided for each car. These batteries consisted of 32 cells, since 64 volts has been the common voltage for head-end systems because of the length of conductors. Head-end systems are still found without storage batteries on some suburban trains which are operated without change in make-up.

Since the voltage of the generator used to charge a battery is above the ordinary lamp voltage, it is necessary to provide some means of voltage regulation to avoid burning out the lamps, except on the constant-potential system. Several different methods have been used, including a resistance in the lamp circuit, an automatic regulator, a three-wire system with the lamps on one side and the battery on the other, a booster set, and finally a paralleling of the two halves of the battery during the charging period.

Head-end systems have found their chief application on trains having long runs from Chicago to the West.

Axle-generator Systems.—Within recent years the system developing most rapidly has been the so-called axle-generator system (Fig. 145), in which each car is provided with a battery and a generator to charge it, driven by the axle of the car. As used in the United States, the axle-generator systems are almost universally of the 32-volt type. In Europe and some parts of Canada, 24-volt systems are common.

The essential parts of the axle-generator system (excepting the constant-potential system described below) are, first, the generator, which usually is of the inclosed type, shunt-wound, and provided with some form of pole changer, unless of constant polarity, in order that its terminal voltage may be the same irrespective of the direction in which the car may be traveling; second, an automatic switch, usually of the solenoid type, to connect the generator with the lighting system and the batteries when the car attains some predetermined speed; third, a

regulating device for controlling the voltage supplied to the lamps and the current to the batteries; fourth, the battery itself, consisting of 15 or 16 cells of the lead-acid type or 25 cells of the alkaline or Edison type; and lastly, some means for limiting the charging of the battery.

The necessity for a regulating device to control the voltage to the lamps may be seen from the fact that a 16-cell battery, when discharged to 1.8 volts per cell, has an effective voltage of 29, while the same battery, at the conclusion of the charging period, will have a voltage of 2.5 to 2.6 volts per cell or 40 to 42 volts for the battery. Increasing the voltage from the 29 volts at the end of the discharge to 34 volts means doubling the illumination furnished by the lamps. Regulators are normally adjusted to limit the voltage to 32 volts at the lamps.

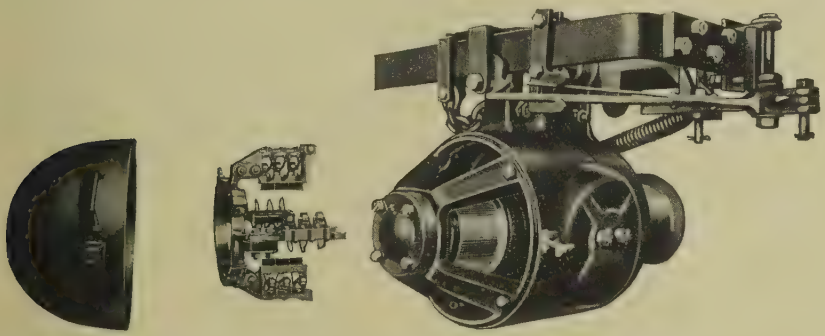

FIG. 145.—Axle generator for car lighting, cover and brushes removed.

The axle-generator systems may be subdivided into two classes, according to the method of charging the battery. These are the constant-current and the constant-potential methods of charging. Some of the constant-current systems comprise a multipolar generator, shunt-wound, of the inclosed type with a pole changer mechanically operated. The automatic switch which connects the generator to the battery is closed by the operation of a solenoid gear. The solenoid is provided with two coils, one being a shunt coil across the generator mains, which serves to close the switch when the voltage of the generator has reached a predetermined value. The series coil of the solenoid becomes energized when the switch is closed and reinforces the shunt coil, except at such times as the voltage may drop to the point where the battery current reverses. Then the series coil opposes the shunt coil, opening the switch. Generator regulation is effected through the compression of carbon piles or the rotating arm of a rheostat. The lamp regulators also consist of carbon piles compressed by the lever arm of

a solenoid, the pressure being inversely as the voltage of the lamp circuit.

A successful application of the principle of constant-potential charging has been made to railway car lighting in the E. S. B. system. The voltage of the generator, when running above the cut-in speed, is held constant at a value slightly above the floating voltage of the battery. Fifteen-cell batteries are used for the 32-volt system, and the control is designed to maintain a terminal voltage of $33\frac{1}{2}$ volts or 2.23 volts per cell, which is below the gassing voltage. (Fig. 146.)

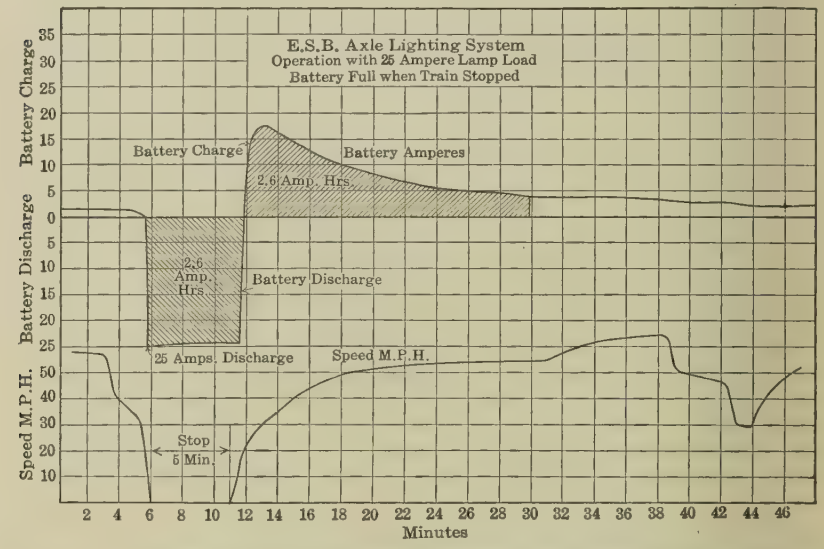

FIG. 146.—Operation of a car-lighting axle generator and battery during and following a train stop. Constant-potential charging.

The generator is of the Rosenberg type, for which the polarity remains the same irrespective of the direction of rotation. The operation of the generator and its control for constant voltage may be studied from Fig. 147. The machine is of the bipolar type, with four sets of brushes at 90° intervals. One pair of these is connected through the series field F^2 to the outside terminals. The other pair is short-circuited. The primary field excitation is provided by a shunt field F^1 connected to the machine terminals through a Wheatstone bridge W, consisting of fixed coils X, and iron resistances Y with a large temperature coefficient. The flux resulting from the primary field passes through the armature in the direction P, return being made through the frame of the machine. A low voltage-difference is created between

the short-circuited brushes, which causes sufficient current to flow in the armature coils to produce a magnetic field of considerable magnitude at right angles to the primary field. This secondary field flux is shown at K. It is cut by the revolving coils on the armature and produces the required voltage at the brushes B^2, which are connected to the terminals of the machine. The Wheatstone bridge is adjusted for balance when the terminal voltage of the machine is $33\frac{1}{2}$ volts, and the points 1 and 2 are then at the same potential. This eliminates the flow of current through the shunt-field coils, the primary excitation being provided by the residual magnetism. If the voltage falls below $33\frac{1}{2}$ volts, the decrease in current through the bridge allows the iron coils to cool. This increases the conductivity of the arms marked Y, unbalancing the bridge and permitting current to flow through the shunt

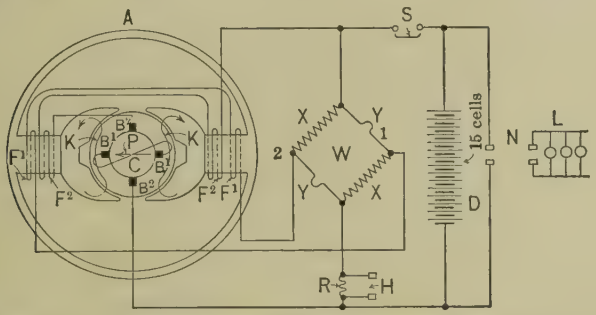

Fig. 147.—Diagram of circuits for train lighting with constant voltage generator for charging.

field, which raises the voltage of the machine until the bridge again balances. At excessive speeds the shunt fields may oppose the residual magnetism. Since the direction of the field K reverses as the direction io rotation of the armature reverses, the polarity of the machine always remains the same.

The advantages claimed for this system are as follows: (1) The battery attains its maximum length of life, because excessive overcharging is avoided. (2) The charging rate varies with the state of charge of the battery. (3) Cost of maintenance is reduced, because cleaning is required less often and flushing may be required as seldom as once in six months or a year. (4) A number of parts are eliminated, including the pole changer, the regulators, and the ampere-hour meter.

d. Operation of Train-lighting Batteries.

The operation of train-lighting batteries follows the general rules for the operation of storage batteries. The daily inspection of batteries

in service consists in specific gravity readings of the pilot cell, and measurement of the temperature and the voltage when the lights are burning. At the end of the charging period for batteries on the straight storage system, readings of the current and voltage of the battery and the temperature and specific gravity of the pilot cell are taken and should be entered in a permanent record. It is necessary, less frequently, to read the specific gravity and voltages of the individual cells in the battery and give the cells an equalizing charge.

The life of the batteries in railroad service will range from two to ten or twelve years. It may be necessary to renew the positive groups, but the negative groups are expected to give a life of ten to twelve years. When the negative groups of the Planté type are deficient in capacity, it is possible to rejuvenate them by a reversal. The plates are assembled with dummies in a pure electrolyte and converted to positives, after which they are again reversed and brought back to the negatives. This treatment expands the active material and increases the capacity. The Edison batteries for car-lighting service usually give a longer life than the lead batteries.

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4. TELEPHONE BATTERIES

Storage batteries form an important part of the telephone power-plant equipment. The requirements of telephone service are very exacting, and much care and engineering skill have been devoted to perfecting the installation and operation of these batteries. The large and most of the small, telephone central offices in cities are operated on what is called the common-battery system in distinction from telephones in isolated communities where each telephone has its own local battery of dry cells. The storage batteries at the central offices

furnish the current for transmitting, signaling, and relay circuits. In addition, they serve as sound absorbers, preventing the "cross talk" of simultaneous messages, and reducing the noise made by the motor-generators or rectifiers which supply current. In most offices the night load is small and the charging machines are shut down, the battery then furnishing the required energy.

Besides the normal uses for these storage batteries, they are required in times of emergency to carry the entire load of the central office. This includes, in addition to the above service, the operation of the ringing circuits and many miscellaneous uses. The batteries are provided with sufficient reserve capacity to permit the operation of the central office to continue for some time after failure of the outside power supply.

a. Description of the Batteries.

The switchboards in the usual type of manually operated offices are provided with a main battery of 11 cells, which is called the "24-volt" battery. In addition to this, there is a second battery of 11 cells in series with the first, this being called the "No. 2" or "48-volt" battery. The whole string of 22 cells furnishes current for toll calls and long-distance messages, and for operating certain types of private branch exchanges. The size of the cells in these batteries will naturally depend upon the amount of traffic which the exchange handles. The 24-volt battery ordinarily consists of cells containing plates $15\frac{5}{16}$ inches by $15\frac{5}{16}$ inches. These are contained in lead-lined tanks mounted on oil insulators similar to those used for a 220-volt system. The plates are usually Manchester positives and box negatives. The number of plates in each cell varies with the requirements of the particular exchange, but space is often provided for the addition of more plates in each cell to take care of the need for increased capacity as the traffic through the office increases. The capacity of cells of this type containing 11 plates is 800 ampere-hours at the 8-hour rate. These cells can be made in sizes up to 75 plates per cell, for which the capacity is nearly 6000 ampere-hours.

In the newer automatic switching offices, for which greater amounts of power are required because of the operation of the switch mechanism in addition to the other circuits, batteries in lead-lined tanks containing plates of the *H* type $30\frac{3}{4}$ inches by $15\frac{1}{4}$ inches are used. The capacity of these cells per plate is double that for the *G* type. The capacities used in these batteries range up to more than 13,000 ampere-hours, which with two batteries in parallel gives capacity at the normal rate up to almost 27,000 ampere-hours used in the largest 2-unit power plants.

The specific gravity of the electrolyte in telephone batteries when they are fully charged is 1.210. The specific gravity being low, the local action at the negative plates and the deterioration of the separators are reduced to a minimum.

The second group of 11 cells in the 48-volt battery usually consists of smaller cells than those in the main battery, since the requirements for toll and long-distance service in the ordinary central office are much less than for local traffic. The cells of this part of the battery are

FIG. 148.—Storage batteries in a telephone central office.

frequently contained in glass jars for use in manual offices. The battery room of a central office is shown in Fig. 148.

The voltage at the terminals of the main battery may vary from 20 volts when discharging at high rates to 28 volts at the end of charge. This variation in voltage does not materially affect the manual telephone service, lamps and other equipment having been designed to operate throughout this range. For machine switching and for repeater equipment, however, the voltage must be closely regulated to meet the exacting requirements of this apparatus. In normal operation the heavy office load during the day is taken from the charging generator with the battery floating across the terminals. The operating

routine is so planned as to keep the battery always sufficiently charged to assume the full load immediately if the power supply fails. In some types of offices the generators are run continuously, carrying all the load, the battery being fully charged for emergency use.

The batteries are installed in ventilated rooms having acid-proof floors, but small batteries may be placed in cabinets. One terminal of the battery is always grounded. This is usually the positive terminal, since the possibility of corrosion of the subscribers' wires and other equipment is thus reduced. When this precaution is taken there is also less likelihood of corrosion of the lead linings in the tanks, which might result in leaks, in the event that accidental grounds should occur on any part of the system.

The switchboards for private branch exchanges are usually fed from the central office, but sometimes they are provided with local batteries of 8 cells, which are floated on battery cable pairs from the central office. Railroad switchboards require batteries of 11 cells. These are sometimes charged from the 48-volt battery at the central office, but in other cases they are charged locally. The largest sizes of private branch switchboards, which are very similar to the central office boards, are provided with an 11-cell local battery and 11 additional cells for toll service, together with local charging equipment.

There are various miscellaneous batteries of small capacity used in the telephone exchanges in addition to the main batteries. One of these is for the operation of the message registers in manual telephone offices. Thirty-nine volts are required, with an allowable range of plus or minus 2 volts. For this purpose, a small battery of 19 cells is provided and kept charged by floating continuously on the 48-volt battery of the exchange. Coin-collecting devices require 110 volts, two batteries of 55 storage cells each, on the positive and negative sides of a grounded line. Connection being made to one or the other of these batteries, the operator is able to collect or return the coins which have been dropped into the slot of the telephone. Since these batteries seldom exceed 6 ampere-hours capacity in a large office, batteries of dry cells may be used for this purpose, and they are economical where the public pay station development is small.

In offices where repeaters are located for use in long-distance transmission, storage batteries are provided for the operation of the vacuum tubes. The current which is used to heat the filament in the vacuum tubes may in most cases be derived from the main 11-cell battery of the exchange. In some cases, however, separate batteries are provided. A second battery to maintain a difference of potential of 125 to 135 volts between the plate and the filament, and thereby cause the elec-

trons to flow from the filament to the plate, is also required. The capacity of this battery may be as small as 6 ampere-hours since it delivers small currents. In main repeater offices, however, where several hundred repeaters are installed, batteries up to 80 ampere-hours, in duplicate, may be employed.

In telegraph offices, batteries of higher voltage are used. These consist of two parts, each of 60 cells, furnishing 120 volts on the positive and negative sides of a neutral ground wire.

b. Charging the Batteries.

The power for charging the batteries is usually obtained locally from one or more sources. The reliability of the power supply is estimated, in order to determine how much reserve capacity in the batteries is necessary in order to insure the continuous operation of the exchange in time of emergency. Where only one outside power source is available, reserve generators that can be driven by gas engines are frequently provided.

The generators for charging the storage batteries are of a special type. Commercial generators cannot be used, since they would produce objectionable noises in the telephone circuits. The charging generators are designed to furnish power at low voltages and high current capacities. The armatures have smooth cores without slots, the windings being banded on the surface. A large air gap between the armature and the field necessitates the use of a strong field, and copper brushes are employed to diminish the resistance in the circuit. The generators charge the storage batteries while the batteries are in use on the telephone circuits.

In smaller offices, rectifiers are employed for battery charging. These are considered more economical than the generators, since they cost less and require less maintenance. Mercury-arc rectifiers of 50 amperes' capacity are available and may be used in parallel when the current exceeds the capacity of one. The smallest offices and private branch exchanges may use rectifiers of the hot-cathode gas-filled type, such as the Tungar and Rectigon rectifiers, for charging the batteries. These are either controlled automatically by voltage relay or ampere-hour meter at the central office, or adjusted so that continuous operation will keep the battery up without subjecting it to injurious overcharging. In the normal routine, the batteries are charged daily or are floated continuously across the terminals of the charging machine or rectifier.

c. The Service that the Batteries Must Perform.

The current drain is determined by (1) the number of calls, (2) whether they originate or terminate in the same office or go to other offices, (3) the resistance of the line, and (4) the average time consumed in the calls. It is difficult to estimate the actual amount of electricity required per call, since all of the above factors vary for each office and vary at different times in the same office. The current for talking, which is transmitted over the wire, is very small; about 1 ampere-

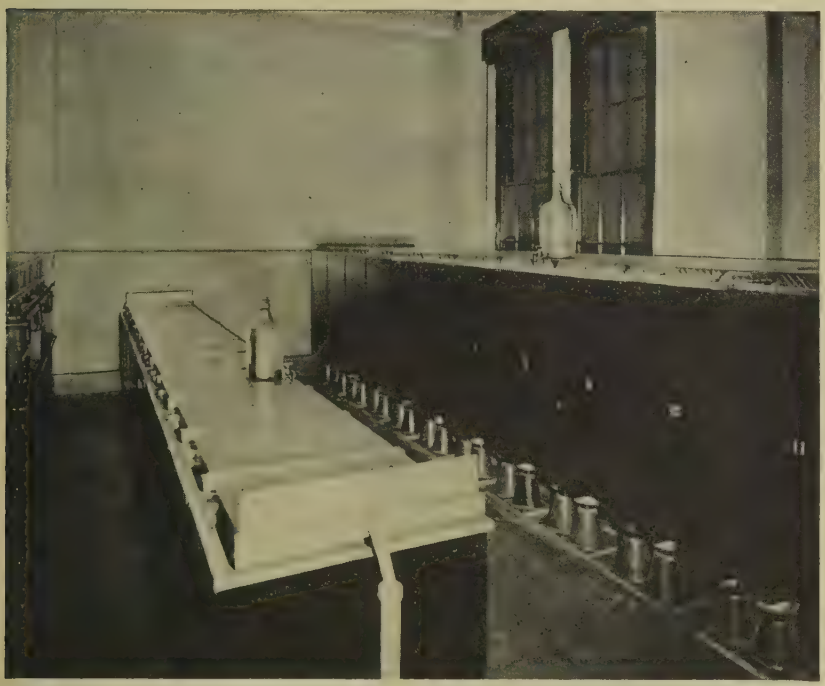

FIG. 149.—Storage batteries for a machine-switching telephone central office.

minute is a rough estimate of the quantity of electricity which is used for performing all the functions required for a call originating and ending in the same local office. Although this quantity is small, very large capacities are required for the batteries, because of the multitude of the calls for which they are required to furnish current.

Absolute reliability of operation is required of telephone storage batteries. They must operate twenty-four hours a day, and it is especially important that the telephone exchange should operate in times of public emergency.

In certain of the newer exchanges where machine switching of

the calls is replacing manual operation, much greater demands are made upon these storage batteries and the capacity must therefore be increased, as previously mentioned (Fig. 149).

From the foregoing it will be seen that the telephone system uses many sizes of storage batteries, practically all sizes in fact, from 6 to 27,000 ampere-hours, for which cells in parallel must be employed. The voltages run from 2 to 150, including telegraph and repeater applications. Nearly all batteries are of the Planté type, since weight and high discharge rates are unimportant, while reliability, long life, and minimum annual costs are desired.

5. ISOLATED ELECTRIC LIGHTING SYSTEMS

The lighting of houses and the operation of small motors and other appliances by electricity, in communities not served by central-station power, has been made possible within recent years by the development of the so-called isolated electric lighting plants. These miniature power plants possess the essential parts of the larger systems. First there must be a " prime mover " or engine of some sort. This is generally a gasoline or kerosene engine with an automatic speed regulator. The next unit is the generator, which is driven by the engine. It may appear as a separate unit connected to the engine by a belt, or it may be directly connected to the engine and appear to be a part of it. The third element of the system is the storage battery, which serves as a reservoir to supply electrical energy whenever it is needed. The battery receives its energy from the generator at intervals, but these miniature generators, unlike those of central stations, are in operation only part of the time. There is also a control panel, although it may be very simple, that provides the necessary switches to connect the generator, the battery, and the distribution system. Ordinarily an ammeter and a voltmeter are provided on this board, and perhaps a regulating resistance to control the charging current. Finally, there is the distribution system.

Electric lighting systems in rural districts present many advantages. First, there is the convenience of electric light and power, a consideration which has brought electricity into very general use at the present time. Second, electricity provides better illumination. The light is much whiter than that given by a kerosene lamp and the quantity of light may be regulated at will by the user, who may select any size of bulb that he may wish. Third, the lighting effects may be made very pleasing and restful to the eyes, by a proper selection of shades and fixtures. Fourth, the system, if properly installed, causes less fire hazard than the use of oil lamps. In country districts, where the pro-

tection afforded by trained firemen and fire-fighting apparatus is not available, this is a factor of great importance. Some thought should be given to the storage of the fuel supply. Tanks of any considerable capacity should be placed below ground. It is often possible to place the plant in a small building, centrally located with reference to the principal buildings which are to be lighted. This is desirable if the battery can be protected from the possibility of freezing.

a. The Wiring.

Low voltages have become standard for the isolated electric lighting system. This makes an economical battery possible. The battery consists of 16 cells of the lead-acid type. The maximum discharge voltage is therefore 32 volts. Since the lower voltage requires an increase in current to provide any specified amount of power, the problem of wiring is somewhat different from that presented by the 110-volt systems which are found in urban districts. Low-voltage lamps and appliances are required. Metal-filament lamps of both the vacuum and the gas-filled types are obtainable at voltages of 28–30 volts. The voltage at the fixture is slightly lower than the maximum at the battery terminals. The various appliances are also rated for the same voltage. The wiring must be larger than for the higher-voltage systems, in order to carry the current without undue voltage loss and without excessive heating. The current of the 32-volt system through a given lamp or appliance is 3.5 times as great as the current of a 110-volt system through a lamp or appliance of the same watt capacity. The voltage drop through a given wire is therefore 3.5 times as great, and the heating effect, which is proportional to the square of the current, is twelve times as great. The size of wire to be used will be governed by the maximum load and the distance between the power plant and the place of utilization. A diagram showing the required size of wire to meet any ordinary conditions has been published by the Engineering Department of the National Lamp Works.[7] The economical solution of the wiring problem requires that the lighting plant be centrally located with respect to the houses and barns and other buildings in which lights or appliances are to be placed.

Although the voltage is low, the insulation standards for 110-volt systems should be followed, because it is then possible to connect to a 110-volt power distribution line that may be put through the locality in the future, without changing anything but the lamps or accessories. The reverse is not true, however, since the smaller wire of the 110-volt systems is not adequate for the low-voltage system.

[7] Bulletin 34, p. 7, 1918.

b. The Battery.

The battery usually consists of 16 cells of the lead-acid type, but Edison batteries are also used for this purpose. The former type have pasted plates $5\frac{3}{4}$ inches wide, $4\frac{7}{8}$ inches high. When larger capacities are required, however, plates $7\frac{3}{4}$ by $7\frac{3}{4}$ inches are used. The number of plates in the small cells ranges from 5 to 23. The capacities for these and for several intermediate sizes are given in Table LV.

TABLE LV

CAPACITY OF ISOLATED PLANT BATTERIES

Number of Plates per Cell	Capacity in Ampere-hours	
	Continuous Rating, 8 Hours	Intermittent Rating, 72 Hours
5	37	53
7	56	80
9	74	106
11	93	133
13	112	160
15	130	186
17	149	213
19	168	240
21	186	266
23	205	293

The positive plates are somewhat thicker than the plates of starting and lighting batteries. The separators are of wood and perforated rubber. The latter being placed between the positive plate and the wood separator, some means is usually provided to lock the element in place to prevent possible buckling of the plates. Whenever possible, it is preferable to use the larger cells, particularly if heating devices, such as electric irons, and motors for power purposes are to be operated. For example, a motor of one horse-power requires 746 watts or 5968 watt-hours during a discharge period of 8 hours. This exceeds the capacity of all but the largest batteries in Table LV. It is possible to minimize the load on the battery by running the charging apparatus during the periods when the power consumption is high. Current can be taken from the battery and generator together.

Batteries of this type are usually contained in glass jars through which the element is clearly visible, but when they are installed on

yachts or required for portable service rubber jars are preferable. The batteries for domestic use are shipped assembled, sealed, and charged. They are ready for immediate use by the purchaser.

c. Rating of the Batteries.

Batteries of this type are given a dual rating by the Standards of the Society of Automotive Engineers. The continuous rating is based on an 8-hour discharge and the intermittent rating on discontinuous discharges covering a period of 72 hours. These ratings have been defined on p. 310, in Chapter IX.

d. Installation and Operation.

The following are the principal points to be observed in installing a battery of this type. Upon receipt of the material, the batteries should be unpacked promptly, the cells being lifted vertically out of the crates, one at a time. Care must be exercised in handling the cells, to avoid breakage. It is not desirable to handle the cells by the terminals or connecting straps. If the crates are carefully opened, they may be used to make a suitable rack for mounting the cells permanently. Figure 150 shows 16 cells mounted in a rack constructed from the packing cases. If a jar has been cracked, the element, consisting of the plates and separators with cover attached, should be removed and placed in an upright position in a wooden pail or porcelain crock filled with pure water until a new jar and electrolyte can be obtained. Before the cells are connected, the ends of the soft lead connecting straps should be scraped to insure good contact, and the cells should be placed on the racks so that the covers are at least $\frac{1}{4}$ inch apart; more space is desirable. The cells must be placed so that the positive terminal of one cell is adjacent to the negative terminal of the next cell, and so on to the end of the row. The cells are then connected by the flexible lead straps. To avoid corrosion, the cell terminals should be wiped clean and dry, and a thin layer of vaseline smeared on each bolted contact. Poor contacts can be detected after several hours, when the battery is in operation, by a rise in temperature.

At one end of the battery there is a positive terminal, and at the other a negative terminal. Connection is made to the external circuit at these terminals, but some care is necessary to avoid corrosion. The copper wires should be stripped of insulation for about 2 inches from the end, the wire made bright by scraping with a knife, and a loop formed through which the stud of the bolt can pass. Before the connection is tightened, vaseline should be liberally applied, and when

the connection is completed the joint should be taped. If corrosion should take place, remove the tape and disconnect the wire so that all metal parts may be cleaned and wiped with a cloth moistened with ammonia water, after which the connection is again made and covered with vaseline.

Although the battery may have been fully charged when it left the factory, part of this charge has been lost because of local action during

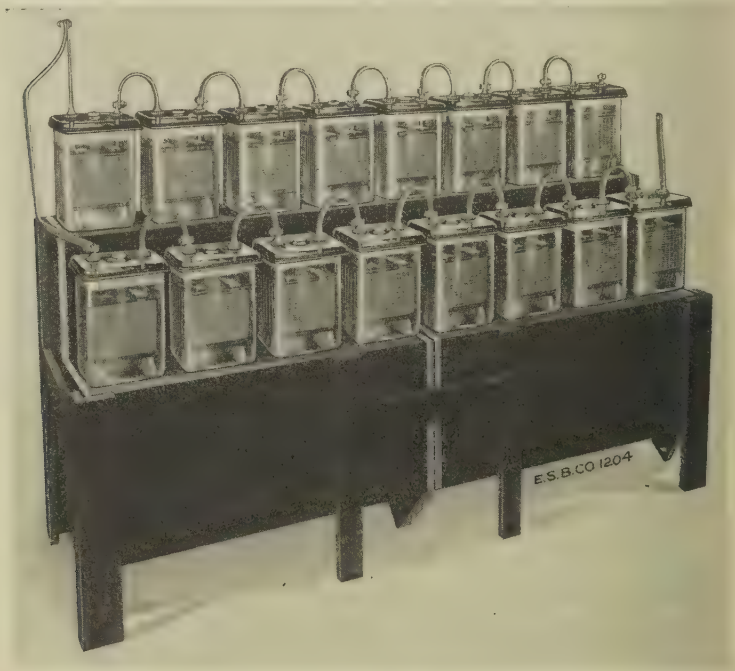

FIG. 150.—Isolated lighting plant battery. The rack for supporting the cells has been made from the crates in which the cells were shipped.

the time of transit, and the battery should be charged at once when the connections to the control panel and the generator are completed. Each cell should be inspected, and sufficient pure water added to bring the level of the electrolyte to the " water line," or to $\frac{1}{2}$ inch above the plates if there is no " water line." The water should be added at the beginning of the charge or soon thereafter.

The proper specific gravity of the electrolyte, when the battery is fully charged, varies somewhat from one make to another. These batteries are not required to deliver heavy currents or to give maximum output within certain weight limitations, and therefore a high specific

gravity of electrolyte is not necessary or desirable. A specific gravity of 1.250 at 75° F. is a maximum. Since cells of the rubber-jar type do not provide as great a space for the electrolyte as other cells of this class, a higher specific gravity of electrolyte, 1.280, is used. Some manufacturers recommend 1.225. Readings of the specific gravity are made with a syringe hydrometer. After each reading is taken, the electrolyte should be returned to the cell from which it was taken. At the end of an equalizing charge (see p. 225) the specific gravities for all cells should be within 10 or 15 points of the same value.

To obtain the best service, only pure water should be used. This should preferably be distilled, but at least it must be free from metallic impurities and excessive amounts of dissolved mineral matter. Rain water may be satisfactorily used.

The observance of certain precautions in the operation of these batteries will greatly assist in making them satisfactory, and prolonging their period of useful service:

1. Charge the battery regularly and sufficiently, avoiding temperatures in excess of 110° F. Charging must be stopped if that temperature is reached.
2. Supply pure water to replace evaporation, as needed. Add the water at the beginning of charge as otherwise it may not mix with the electrolyte and may freeze if the temperature of the room is low.
3. Avoid allowing the battery to stand in a discharged condition. The sulphate on the plates becomes more difficult to reduce if the battery is neglected. A discharged battery may freeze (relation of specific gravity to freezing point given in Fig. 38). There is no danger of a fully charged battery freezing.
4. Never add acid to the battery unless acid has been lost by spillage or otherwise. If the specific gravity is low, the battery probably needs charging. The electrolyte is a solution of pure sulphuric acid. Other substances and solutions " recommended " for various real or imaginary troubles should be avoided.
5. The place where the battery is installed should be kept clean and dry. The holes in the vent plugs of each cell must be open to permit the escape of gas when charging. The gas is explosive, and therefore any open flames, or lighted cigars or cigarettes in the vicinity of the battery should be avoided.

6. If a jar is broken or the electrolyte needs changing because of impurities that may have gotten into the cell, the element should be removed and immersed in pure water in a wooden pail or earthenware jar until the cell can be assembled again. The plant can be operated temporarily with one cell removed.
7. Electrolyte which has been spilled should be neutralized with soda and wiped up. It will not dry up unless neutralized, because sulphuric acid is hydroscopic.
8. If the sediment in the bottom of the jars reaches the bottom of the plates, the cells must be disconnected, disassembled and cleaned. The electrolyte can be syphoned off the sediment and used over again. During this process the plates and separators should not be exposed to the air for more than a few minutes at a time, because the negative plates may oxidize and become hot.
9. If the battery is to be idle for several months, it should be given the necessary water, then fully charged, and finally disconnected at the terminals from the rest of the circuit. When the period is to be longer than six months, the battery should be disassembled and put in dry storage. To do this, charge the battery fully; disconnect the cells; remove the element of each with the cover attached; pour out the electrolyte and save it in a non-metallic vessel; wash the jars and refill them with water; soak the element of each cell in the water for a period of five hours; remove the elements to drain and dry and throw away the water. The dry elements may be stored by putting them back in place in the empty jars. To restore the battery to service the old wood separators must be carefully removed and replaced by new separators; the elements are then put in position in the jars and the old electrolyte added (new electrolyte should be of the same specific gravity as that which was previously removed). After the cells are assembled and the electrolyte in them, they should be allowed to stand for about twelve hours before being charged. The first charge may require several days but need not be continuous. Charging should continue until the specific gravity has ceased to rise. It should reach the same value as previously observed at the end of full charge.

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6. RAILWAY SIGNAL BATTERIES

The most important invention for the promotion of safety, in the history of railway transportation, was the invention of the closed track circuit. The automatic operation of signals by means of the track circuit involves the use of several batteries. Primary batteries have been used for this purpose in isolated communities, but the use of the storage battery is growing with the extension of electrical power transmission lines and the development of small rectifiers for battery charging. At the beginning of 1921 there were 61,744 miles of track equipped with automatic block signals.

The closed track circuit was invented by Dr. Wm. Robinson, August 20, 1872. This invention grew out of his previous invention of the so-called "open track circuit" for railway signaling, which proved to be unsatisfactory because it was possible for the signals to indicate that the track was clear when such was not the case. This might happen in several ways, as for example, if a train should break in two, leaving one part within the block, or if a train should enter from a siding or from the other end without setting the signal to danger. Furthermore, the failure of a wire or of a battery would, without warning, render the open-circuit system inoperative.

The closed track circuit differs from the open circuit in the essential particular that a small electric current flows continuously from the battery through a section of the track, and, when the track is clear, the signal is held at the safety position by the flow of current. When a train enters the block, the wheels and axles of the engine and cars short-circuit the track relay and release the signal, which immediately falls to the danger position, by the action of gravity. Every pair of wheels on the train controls the signal throughout the entire block, and the causes of possible failure of the open track circuit are eliminated.

In Fig. 151 a diagram of the simplest closed track circuit is shown. The battery at one end of the section causes a current to flow through the track to the other end of the section, where it traverses the coils of a relay and returns through the second track to the battery. The magnet of the relay is normally energized and the signal held in a clear position. Each section of track is separated from the adjacent section by insulated joints. The signals which are controlled by the relay

may be of various kinds, including those operated directly by electric motors, and electrically controlled, pneumatic, or fluid pressure systems. The actual kind of signal is immaterial, as the general principle of operation of the signal system is the same for all. The train entering the block connects the rails, short-circuiting the relay and causing its armature to fall and thereby release the mechanism controlling the signal.

The simple system represented by Fig. 151 was extended in 1876 to the case of a double track circuit having switches within the block. Dr. Robinson was able to condition the indications of the signals upon the closing and locking of each switch in the proper position before a clear track could be indicated. From this has grown the elaborate

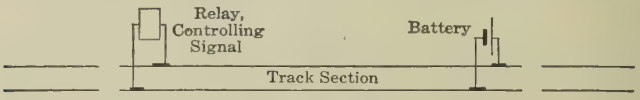

FIG. 151.—Simple closed track circuit.

interlocking systems for controlling complicated networks of track, such as we have at the present time.

The present high state of development of the signal systems has not been brought about without the necessity of overcoming serious engineering difficulties. The conduction of the track is a variable factor. Rust accumulates between the plates and the rails at the joints, increasing the resistance. To overcome this Dr. Robinson invented the bonding of the rails in 1872. Long wet tunnels, in which the insulation between the tracks is poor, and roadbeds saturated with brine from refrigerating cars, allow large leakage currents to pass between the rails. The preservatives, such as zinc chloride, used for treating the ties to prevent rotting and the attacks of insects, make the ties sufficiently conducting when new to interfere with the signal circuits if more than about 15 per cent of these ties are installed within any one track circuit within a year. These difficulties have been overcome and the operation of the signal systems made effective.

The batteries for operating the relays and signals are usually located in cells or boxes by the side of the track. Only a low voltage—1 to 2 volts—is required for the track circuit, but 8 volts are necessary for the signals.

The track sections constituting the blocks vary somewhat in length, but are usually from $\frac{3}{4}$ to 1 mile. The rail resistance is normally about 0.200 ohm per thousand feet and for this reason it is necessary to place a resistance in series with the battery, especially in the case of

storage batteries, to prevent the flow of excessive currents when a train is on the track. The resistance of the track relay is either 2 or 4 ohms. Temperature changes produce marked variations in the resistances of the track circuit, because the temperature coefficient of the steel rails is large. The condition of the roadbed, whether wet or dry, is an important factor also in determining the amount of current which flows from the battery. Normally, the battery current is from 400 to 500 milliamperes, increasing to about 1.8 amperes when the train is on the track. The length of time that this heavy current flows will depend upon the kind of train passing the block; $1\frac{1}{2}$ minutes for express trains, and 4 minutes for freight trains, on the average.

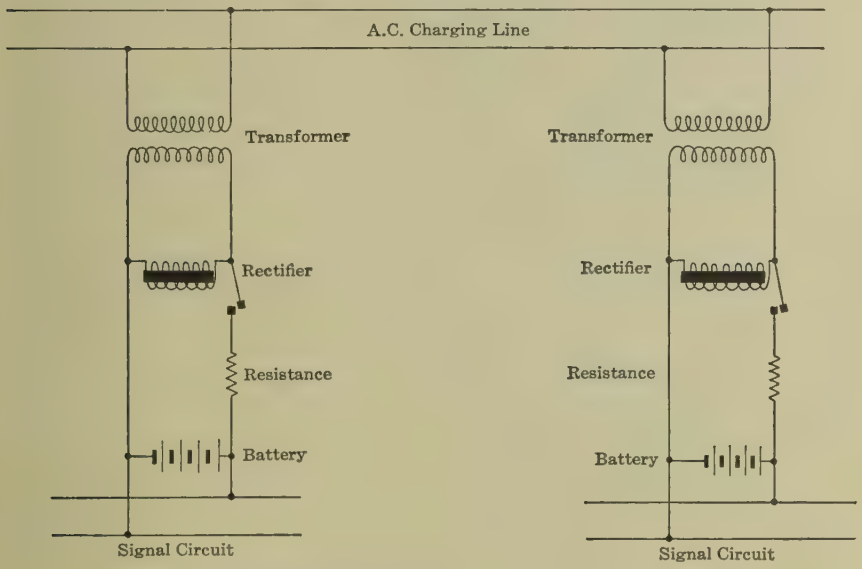

FIG. 152.—Floating battery system for railway signal circuits.

The batteries for the track circuit consist of one or more storage cells in parallel, each having a capacity of about 75 ampere-hours. The charging of these batteries may be accomplished in either of two ways. They may be collected and replaced at intervals for charging at a central station, or they may be charged by a trickling current, usually obtained from a mechanical rectifier of the vibrating-reed type. (Fig. 152.) In making an estimate of the cost of operation of the track battery, the following factors must be taken into account:

First, the initial cost of the battery;
Second, the maintenance required, and

Third, the cost of the charging current at the terminals of the rectifier.

The signal circuit usually includes 4 storage cells in series, of about 75 ampere-hours capacity. A single cell from a battery used for this purpose is shown in Fig. 153. These cells are required to clear the signals, that is, to raise the indicator from the danger position to the clear position when the train passes out of the block, and to hold the signal clear until the track is again occupied. From 2 to $3\frac{1}{2}$ amperes, depending on the type of signal, for 10 seconds, are required to clear and 25 milliamperes are required to hold the signal. An average number of operations of a signal per day is 40, but this depends on the traffic.

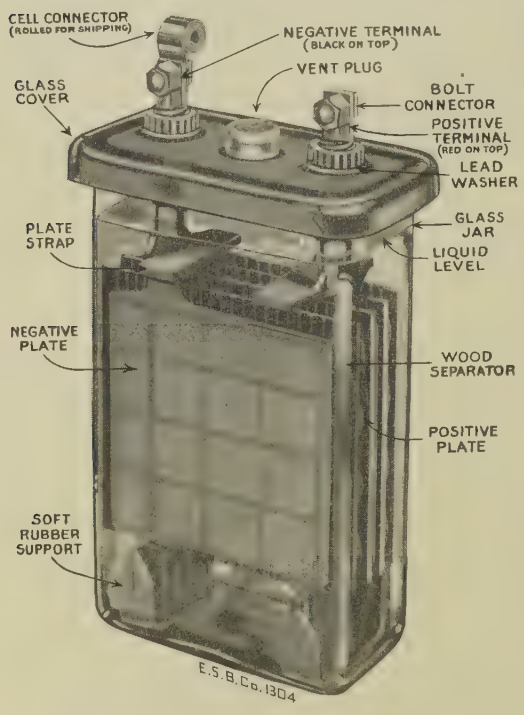

Fig. 153.—Railway signal cell.

These batteries contain heavy plates about $\frac{1}{4}$ inch thick and have a relatively low specific gravity of electrolyte. Such a battery offers maximum strength and durability and small losses from local action within the cells.

Reliability of operation under hard service conditions is the first essential of these batteries. They are protected from the weather, but subjected to severe changes of temperature and moisture.

There are also other uses for storage batteries in connection with railway signaling and similar work. These include batteries for the operation of crossing bells, wigwags, the lighting of signal lamps, and the operation of track switches. Larger batteries of the stationary type, both lead and Edison, are found in signal towers for the operation of a large number of relays and track switches. The stationary storage batteries in the signal towers are charged by a local

generator driven by a gas engine, if a power circuit is not available.

A great increase in the use of storage batteries for railway service will probably come with the installation of train control devices. Although there are a number of systems which have been invented for automatic train control, nearly all that are being investigated at the present time involve a storage battery, either on the locomotive or beside the track.

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7. BATTERIES FOR RADIO RECEIVING SETS

The operation of electron tubes for radio receiving requires two batteries. One of these (the "A" battery) furnishes the current to heat the filament of the tube to incandescence and thereby cause it to emit electrons. The other battery (the "B" battery) is used to maintain the plate at a positive potential with respect to the filament, which causes the negatively charged electrons emitted by the hot filament to flow to the plate. Between the filament and the plate is interposed a grid whose fluctuating potential controls the flow of electrons and therefore the flow of electric current through the tube. The potential of this grid changes as the signals are received. (Fig. 154.)

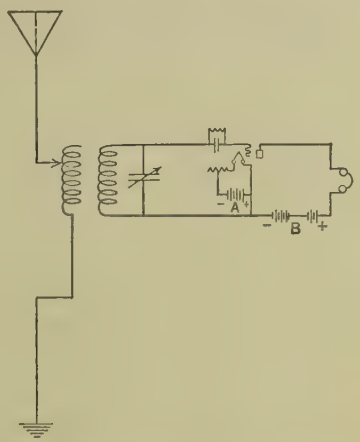

FIG. 154.—Simple radio receiving circuit, showing the position of the A and B batteries.

"A" batteries supply 6 volts and a current ranging from a fraction of an ampere to several amperes, depending on the number and type of the tubes. Storage batteries are well adapted to this purpose. A 3-cell battery of the starting and lighting type for automobiles, having a capacity of 60 ampere-hours or more, can be used, but batteries especially designed for radio service are now available and are better adapted to the purpose. Radio batteries are not intended to deliver the large currents required of the automobile batteries. They can,

therefore, be made with thicker and more durable plates, and with smaller terminals, which decrease the weight. They may contain electrolyte of relatively low specific gravity, such as 1.250, and thereby decrease the local action taking place within the cells. Radio batteries resemble in size and appearance the starting and lighting batteries for automobiles. They are sometimes sold in the dry condition; that is to say, they are not filled with electrolyte until the battery is purchased, when it is filled and given a preliminary charge. In the case of a few makes, the plates are sufficiently charged to make the battery operative when the electrolyte is first poured in. The latter do not develop their full capacity on the first cycle, however, and it will be noticed that the capacity of these batteries will increase during the first few cycles of use.

No ratings for storage batteries of the radio type have been standardized. Manufacturers' catalogues specify ampere-hour ratings, but it is difficult, if not impossible, to compare exactly the capacities of different makes on this basis because of the lack of a standard method for deriving the ratings. Various sizes of the batteries are available and any of them, even the smallest, can be used for the largest receiving sets if recharged sufficiently often.

The charging of the radio batteries is usually done at home. If direct current is available, a suitable regulating resistance may be made from a bank of incandescent lamps. If only alternating current is available, a rectifier must be used to change it to direct current. Electrolytic rectifiers, mechanical rectifiers of the vibrating-reed type, or gas-filled bulb rectifiers may be employed. It is not necessary that the rectifiers should charge the battery at the normal charging rate. A lower rate is entirely satisfactory if the charging period is continued long enough for the battery to acquire a complete charge. In addition to charging, radio batteries require the addition of pure water from time to time to replace the loss of water that occurs because of evaporation and the gassing of the batteries while on charge. Distilled water is preferred for this purpose.

The second battery required for the operation of radio receiving sets, commonly called the " B " battery, is frequently composed of dry cells, but a number of different types of small storage batteries, having 12 cells and giving 24 volts, have recently appeared upon the market. These are of a great variety of sizes and kinds. (Fig. 155.) The B battery of the storage type possesses some advantages over the dry-cell battery for this purpose, but requires more care. The drop in voltage of the storage battery from the fully charged state to the fully discharged state is from 24 volts to $21\frac{1}{2}$ volts or 10 per cent, while the drop in volt-

age of the battery made up of 15 dry cells is from 22.5 volts to 17, a drop of nearly 25 per cent. The radio B batteries need careful attention because of their small size. Pure water must be added frequently by means of a medicine dropper. The charging of the B batteries presents somewhat more difficulty than that of the A battery. If direct current is available, the B battery may be connected in series with an incandescent lamp and the 110-volt supply. If alternating current only is available, a small type of rectifier must be used. When

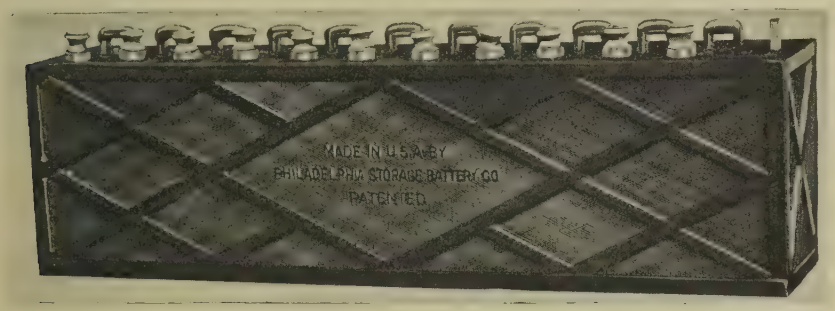

FIG. 155.—Radio B battery

this is the case, a tungsten lamp is connected in series with the 110-volt circuit and to this is connected a rectifier, such as the electrolytic type, and the storage battery.

8. CENTRAL-STATION BATTERIES

The character of the service required of central-station batteries has changed during the last few years and this has brought about a change in the type of battery and the method of its operation. In the early days of electrical engineering, central stations were confronted with heavy loads at certain times of the day and light loads at other times. The load factor was low and efforts were made to improve the efficiency of operation by the use of batteries. The storage battery is particularly well suited to equalize an uneven load because of its ability to receive energy at one time and deliver it at another. The first central-station battery in this country is said to have been installed in 1885, and in the years that followed many battery installations were made. The primary purpose of these batteries was to assist in carrying the heavy, or "peak," loads, the battery receiving its store of energy at such times as the generating equipment could carry the external load and charge the battery too. In some installations, when the mini-

mum load was too light to operate the generators efficiently, the battery was used to carry the entire load for part of the time. The batteries were charged and discharged daily and it was necessary, therefore, that they should be provided with rugged plates of long life. Planté plates were commonly employed, and the output of the cells for the space which they occupied was relatively small.

Within recent years, advances have been made in both the power and reliability of steam and electrical generating equipment, and the load factor has greatly improved. It is possible now to operate boilers under forced draft when necessary, and the modern generators can carry overloads for sufficiently long times to pass the peak. The necessity for the storage battery in central stations, as it existed some years ago, has practically vanished, but at the same time a new demand for central-station batteries, particularly in the downtown districts of the large cities, has arisen because of the increased importance of continuity of service. One argument in favor of direct-current distribution systems in thickly populated districts has been the possibility of insuring continuous service by the use of batteries held in reserve. The necessity for maintaining lights on business thoroughfares and in places of public assembly, and for the uninterrupted operation of telephones, elevators, underground railroads, etc., can hardly be overestimated. The storage battery is peculiarly well adapted to insure continuous operation, because it has no moving parts and because, when an emergency arises, it can pour its store of energy into the line at enormously high rates of discharge, without delay.

The central-station batteries of to-day are primarily for stand-by service. Figure 156 is a photograph of a modern installation.

The battery for stand-by service is seldom used, but in emergencies it is required to carry the full load, which means discharge at high rates. It must always be charged and ready to assume the load at any moment that the generators may fail; for this reason the stand-by battery usually floats on the line. Its capacity is specified at a very short time rate, such as six or seven minutes. It has been stated that the emergency discharge rate of the numerous stand-by batteries of the light and power companies in New York City in 1923, for a period of six minutes, was 2,125,000 amperes at 125 volts.

Because the battery is seldom used, and then at high rates of discharge for which the maximum obtainable capacity is desirable, the batteries with Planté plates are now being superseded by batteries with relatively thin pasted plates. These batteries are less durable than those with massive Planté plates, and they would not be well adapted for daily discharges as in the case of peak load batteries, but for stand-by

service they have proved satisfactory. The greater rate of depreciation on the pasted-type batteries as compared with the others is compensated by the saving in initial cost and decreased bulk. The pasted-plate batteries give about $2\frac{1}{4}$ times the capacity at emergency rates that the older types of cell could give. The decreased bulk is an important item when these batteries must be installed near the center of congested districts where land values are high.

The batteries ordinarily contain 150 cells, one-half of which are on

FIG. 156.—Central-station battery.

each side of the neutral of a three-wire line. The cells vary in size from those of 29 plates per cell to the very large cells containing 169 plates per cell. Cells containing 141 plates are the ordinary maximum. The dimensions of the plates have now been standardized as follows: width, $15\frac{5}{16}$ inches; height, $30\frac{3}{4}$ inches; thickness, positives $\frac{7}{32}$ inch, negatives $\frac{3}{16}$ inch. In places where floor space is not too valuable and relatively small capacity is required, plates of one-half the height of these are used, because the shorter path for the current gives a slightly better voltage characteristic. The separators are of wood and the standard spacing

of the plates is $\frac{9}{16}$ inch between plate centers. The specific gravity of the acid used is about 1.210 when the battery is fully charged. The cells are contained in lead-lined wooden tanks which are necessary for the larger sizes of cells because of their great weight. Even in the smaller sizes of cells for stand-by service, the tanks are preferable to glass jars because they are not liable to breakage.

The insulation of the cells is of particular importance where the distribution system is grounded to avoid corrosion of the tanks. Insulators used to support the cells are usually glass bodies with an annular trough filled with oil and protected by a lead-alloy cap hanging free of the sides to keep dirt and moisture out of the oil.

The design of the conductors to lead the current out of the cells requires particular care, because it is necessary to work the plates equally and provide sufficient conductivity for the large currents required at times of emergency. The bus-bars on the sides of the cells, at ends of rows, and on the regulating cells are often reinforced by copper bars embedded in the lead. By this means the conductivity can be increased and uniform current distribution to the various plates provided. The conductors leading from the cells are ordinarily copper bars with bolted joints, supported from the ceiling. The attractions and repulsions between these conductors are strong when they are carrying heavy currents and, therefore, a rigid construction is necessary. Less protection is required now than formerly from the corrosion produced by acid spray, for the reason that the batteries are kept floating on the line with very little gassing. In places where the gassing is strong, the copper is covered with a lead sheathing, but a high-melting-point grease or acid-resisting paint may be sufficient.

Regulation is obtained by the use of end-cell switches in an outside room adjacent to the battery. If fine regulation is required the steps may be by single cells; but in emergencies it is usually necessary to cut in the cells very rapidly, and therefore groups of two or more cells may be connected to the successive points of the switches. Four end-cell switches are provided for each battery, two being used on each side of the three-wire system. The two switches on each end are operated in parallel, but each is capable of carrying the load, so that in case of failure of one switch, the other may be used. With the changed character of the service, there has been a change in the requirements and design of these end-cell switches. The current required of the battery may be 40,000 amperes or more in emergencies, and the voltages across the successive points are higher than formerly. The newer switches have contact points consisting of copper, and adjacent carbon and graphite

contacts also, to provide necessary resistance in the circuit as the switch passes from one group of cells to the next. The switches are motor-driven by semi-automatic control, except that the motor may stop only when the switch is upon a copper contact point.

In discharging the batteries at high rates, the final voltage per cell is taken as 1.24 volts at the 10-minute rate.

As the batteries usually float continuously on the line, they are normally fully charged and ready for emergencies. Once a week, however, they are given an equalizing charge for about one hour at about the 10-hour rate. The purpose of this is to bring up any cells that may be slightly below the others, and at the same time to provide an opportunity for a cell-to-cell inspection of voltage and gassing. This charging is usually done late at night when the load is at a minimum and breakdowns are less likely to occur. The charging is done by means of a booster connected in series with the station bus, to give sufficient voltage at the battry terminals to effect the charge.

About once in six months, a test discharge is made during the middle of the night, to give further information about the condition of each individual cell. The line is protected during this period by other batteries in other stations connected to the same network.

The life of these batteries is dependent very largely on the life of the positive plates. In some cases the negatives may outlast the positives; but this is not usual, and the advisability of continuing such plates with a new set of positives should be most carefully considered. Ten years' service and upwards may reasonably be expected from one set of plates. This will depend somewhat on the amount of service required. The maintenance cost for stand-by batteries is stated to be about 3 per cent per year of the initial cost of installation.

Besides the large batteries for stand-by service in central stations, there are other batteries for important uses. Exciter batteries are provided in large central stations to guard against the damage that would result from failure in the field circuits of the generators. Exciter batteries are therefore one type of stand-by batteries designed for use in the power station itself at times of emergencies. Exciter batteries are generally calculated to carry the maximum load for excitation for a period of one or two hours. Another battery is usually provided for the operation of remote-control switches and signal lamps.

Other batteries of the stationary type include the following: load-regulating batteries, which are located near the generator for the purpose of taking up momentary fluctuations; peak-load batteries, also located near the generator to help carry the load during periods of high power consumption; line batteries, usually located at a point

remote from the power house and connected across the line to improve the line voltage, particularly in electric railway work.

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